Final Technical Report

Energy Efficient Removal of Volatile Organic Compounds (VOCs) and Organic Hazardous Air Pollutants (o-HAPs) from Industrial Waste Streams by Direct Electron Oxidation

Performed under Award DE-EE0003494

Project Period 08:2010 – 08:2011

Principal Investigator

Anne L. Testoni, PhD

(978) 658-8600

atestoni@aeb.com

Awardee

Advanced Electron Beams, Inc.

301 Ballardvale Street

Wilmington, MA 01887-4405

October 19, 2011

Acknowledgment

This report is based upon work supported by the U. S. Department of Energy under Award Number DE-EE0003494.

Disclaimer

Any findings, opinions, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the Department of Energy.

Document Availability

Reports are available free via the U.S. Department of Energy (DOE) Information Bridge Website:
<http://www.osti.gov/bridge>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and Informational Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information

P.O. Box 62

Oak Ridge, TN 37831

Tel: (865) 576-8401

FAX: (865) 576-5728

E-mail: reports@osti.gov

Website: <http://www.osti.gov/contract.html>

Table of Contents

List of Acronyms & Symbols	5
Lists of Figures	6
List of Tables	8
List of Appendices	9
Introduction.....	10
Background.....	13
Thermal Energy versus Electron Energy	13
Previous Experiments by AEB	14
AEB Qualifications for Project.....	15
Statement of Project Objectives (SOPO).....	15
Project Results	18
Air Treatment Unit System: Construction & Characterization (Task 3)	18
VOC/o-HAP Delivery Methods Development (Task 4).....	19
Analytical Methods	20
Experimental Protocols (Task 4).....	20
Data Analysis	20
Dose-Destruction Results.....	21
Discussion of Results.....	Error! Bookmark not defined.
Benefits Assessment	26
Analysis Strategy	26
Energy, Environment and Cost Benefits.....	27
Other Benefits	27
Commercialization.....	30
Market & Applications Development	30
Engineering Development.....	30
AEB Commercialization Plans	30
Accomplishments.....	31
General	31
Publications	31
Student Work	31
Conclusions and Recommendations	32
References.....	33

Appendices.....	34
Cost and Energy Benefits Models.....	34
Applications Benefit Model.....	34
Adoption Benefits Model.....	36
Data Compendium #1: Gas Chromatograms for all Compounds	37
Data Compendium #2: Gas Chromatography Retention Times and Mass Spectra of All By-Products	43
Data Compendium #3: VOC removal versus treatment conditions with linear model overlay	46

List of Acronyms & Symbols

AEB	Advanced Electron Beams
ATU	Air Test Unit
CO	Catalytic Oxidation
DEP	Department of Environmental Protection (a function within each state)
DOE	United States Department of Energy
EBO	Electron Beam Oxidation
EIA	U.S. Energy Information Administration
EPA	United States Environmental Protection Agency
GC/MS	Gas Chromatography with tandem Mass Spectrometry
ITP	Industrial Technology Program
kGy	kiloGray = 1000 Gray. 1 Gray = 1 joule absorbed by 1 kilogram
o-HAP	Organic hazardous air pollutant
RCO	Recuperative thermal oxidizer
RTO	Regenerative thermal oxidizer
TO	Thermal oxidation, thermal oxidizer
VOC	Volatile organic compound

Lists of Figures

Figure 1. Distribution of electron beam energy (dose) into air	16
Figure 2. Distribution of dose for two electron beams irradiating across an air gap	16
Figure 3. Configuration of initial laboratory experiments	17
Figure 4. Relative easy of destruction of compounds from initial laboratory experiments	17
Figure 5. Finite element flow model output of the ATU showing improved flow: a) before modifications; b) after modifications	22
Figure 6. Air speed map across the reaction zone for three different volume flows	22
Figure 7. a) Configuration of electron beams in simulation set-up; b) visible light emission indicating electron dose across reaction zone	22
Figure 8. Dose Map across the reaction chamber air flow zone	23
Figure 9. Project equipment configuration: ATU & nebulizer with pump	23
Figure 10. Project equipment configuration: nebulizer & analytical equipment	23
Figure 11. Linear First Order Model applied to data from pine turpentine	24
Figure 12. Linear First Order Model applied to data from benzene	24
Figure 14. Example calculation of using Applications Benefits Model	35
Figure 15. Snapshot of Adoption Benefits Model	36
Figure 16. GC/MS – mineral spirits.....	37
Figure 17. GC/MS – pine turpentine.....	37
Figure 18. GC/MS – benzene.....	38
Figure 19. GC/MS – toluene.....	38
Figure 20. GC/MS – o-xylene.....	38
Figure 21. GC/MS – ethyl benzene.....	39
Figure 22. GC/MS – styrene	39
Figure 23. GC/MS – naphthalene 1:1 in ethanol.....	39
Figure 24. GC/MS – methanol	40
Figure 25. GC/MS – ethanol	40
Figure 26. GC/MS – n-butanol	40
Figure 27. GC/MS – s-butanol	41
Figure 28. GC/MS – t-butanol	41
Figure 29. GC/MS – acetone	41
Figure 30. GC/MS – methyl isobutyl ketone	42
Figure 31. GC/MS – ethylene glycol 1:1 in ethanol	42

Figure 32. GC/MS – butyl cellosolve	42
Figure 33. MS Identification of by-product – acetone.....	43
Figure 34. MS identification of by-product – butanal.....	43
Figure 35. MS identification of by-product – methanol	43
Figure 36. MS identification of by-product – methyl nitrate	44
Figure 37. MS identification of by-product – butanone (MEK)	44
Figure 38. MS identification of by-product – butyl formate.....	44
Figure 39. MS identification of by-product – benzaldehyde	45
Figure 40. Data & Model for Mineral Spirits Figure 41. Data & Model for Pine Turpentine.....	46
Figure 42. Data & Model for Toluene Figure 43. Data & Model for Ethyl Benzene.....	46
Figure 44. Data & Model for Benzene.....	46
Figure 45. Data & Model for o-Xylene Figure 46. Data & Model for Styrene	47
Figure 47. Data & Model for Methanol Figure 48. Data & Model for Ethanol.....	47
Figure 49. Data & Model for norm-, sec- and ter-Butanols.....	47
Figure 50. Data & Model for Acetone Figure 51. Data & Model for Methyl isobutyl ketone	47
Figure 52. Data & Model for Butyl Cellosolve	48

List of Tables

Table 1. Compilation of Emissions of Non-Halogenated VOCs & o-HAPs	11
Table 2. Types of Thermal Oxidizers	11
Table 3. List of chemicals studied in previous experiments	16
Table 4. Electron beam and air flow conditions for VOC/o-HAP experiments	24
Table 5. Summary of dose required to achieve >90% destruction of VOCs/o-HAPs	25
Table 6. Comparison of Energy Use, Costs and CO ₂ Production between RTO & EBO.....	28
Table 7. Conservative projection of domestic benefits of EBO adoption through 2022	28

List of Appendices

Linear Model for Determining Critical Dose

Cost and Energy Benefits Models

Data Compendium #1: Gas Chromatograms for all Compounds

Data Compendium #2: Gas Chromatography Retention Times and Mass Spectra of All By-Products

Data Compendium #3: VOC removal versus treatment conditions with linear model overlay

Introduction

Volatile organic compounds (VOCs) and other organic hazardous air pollutants (o-HAPs) are common by-products of industrial processes in the United States and around the world. These materials are used in industries such as consumer & industrial product packaging, printing & coating, petroleum refining, food & beverage production, forest & paper products manufacturing and organic chemical production. Table 1 shows the common non-halogenated VOCs and o-HAPS by industry and relative emission quantity. Note that this list includes the full range of organic compounds including aliphatic and aromatic hydrocarbons, alcohols, ethers, acetates, aldehydes, and ketones. When introduced into the environment the organic waste products react with air when exposed to sunlight and are a major source of ground level ozone (smog). The o-HAPs also can cause significant human health issues including cancer, asthma and birth defects.¹ Because of these environmental and health effects the emission of these compounds is tightly regulated by the US Environmental Protection Agency (US-EPA). Current US-EPA regulations under the Clean Air Act require capture, recycling or destruction of VOCs and o-HAPs; destruction is the most common choice of control.

The destruction of VOCs and o-HAPs is traditionally performed using high temperature (1600-2200°F) thermal oxidation (TO); the chemical reaction transforms these compounds to more benign species such as water (H₂O) and carbon dioxide (CO₂). The chemical reactions that are occurring can be summarized as follows:

While the thermal oxidation process is very effective – destruction efficiencies greater than 98% can be achieved using high temperatures – the amount of CO₂ generated from burning the fossil fuel can exceed the initial organic pollution by a factor of 10 or more. Small manufacturers producing as little as 3000scfm of VOC-laden air, as would be typical of a regional printing & coating facility, can spend up to \$100,000 per year on natural gas depending upon the type of thermal oxidation equipment present in the factory. Major manufacturers such as chemical factories, automotive paint plants, and food & beverage can production lines can spend more than \$1,000,000 per year in energy to power their thermal oxidizer systems. The four major categories of commercial thermal oxidizers are described in Table 2.

Published external laboratory work²⁻⁸ using static polluted air treated with high energy electron beam systems and proprietary AEB-sponsored research on low volume flow polluted air using its modular, low energy electron beam systems have shown that direct electron energy can induce the same net chemical reactions but at room temperature and with 100% efficient energy transfer between the electron source and the polluted air. Total energy savings of up to 90% have been predicted. A more detailed investigation using realistic air flow model systems was required to validate the published work and determine if direct electron oxidation is an economically viable alternative to thermal oxidation.

In this project we studied how the direct energy from modular, low energy industrial electron beam emitters can drive the oxidation of the organic compounds at room or process temperature. Only small amounts of CO₂ from the destroyed pollutant are generated, resulting in major reductions of greenhouse gas emissions from this process. Since only electricity is required to achieve pollution destruction, a wide range of energy sources, including those which do not generate CO₂, can be exploited. The potential benefits to domestic industry include savings in energy, greenhouse gas emissions, and overall operating

expense.

Table 1. Compilation of Emissions of Non-Halogenated VOCs & o-HAPs

Compound	Annual Emissions by Industry, tons per year										
	Commercial Cooking	Degreasing	Dry Cleaning	Graphic Arts	Chemical Manufacturing	Petroleum Refining	Solvents Non-Industrial	Coatings Architectural	Coatings Industrial	Total	Cumulative % of Total
*Methanol	0	368	3	7785	5992	591	102116	4928	24821	146604	21%
*Toluene	556	4709	4	12165	2712	1573	34683	11518	47340	115260	39%
*Xylenes††	73	13	1854	13409	993	1317	37093	12645	33276	100673	54%
Methyl Ethyl Ketone	0	1366	0	1817	0	0	3759	6698	58972	72612	65%
*Methyl Isobutyl Ketone	0	36	0	557	317	90	679	1469	66224	69372	75%
*Benzene	1222	518	0	342	448	631	54293	445	0	57899	84%
Ethylene Glycol†	0	20	0	861	547	0	0	24784	3485	29697	88%
*Glycol Ethers	0	20	0	861	3387	0	0	24784	4498	33550	93%
Hexane	64	656	0	393	213	1277	6600	1262	1120	11585	95%
*Ethyl Benzene	89	16	1	199	0	198	5466	1287	2303	9559	96%
*Naphthalene	74	25	0	0	1745	218	3344	219	350	5975	97%
*Styrene	456	150	0	0	0	0	0	489	939	2034	97%
Dibutyl Phthalate	0	0	0	2288	279	0	0	0	0	2567	98%
Formaldehyde	973	11	0	0	0	147	71	0	358	1560	99%
Total	3507	7908	1862	40677	16633	6042	248104	90528	243686	658947	

†† includes mixtures and individual emissions for ortho, meta and para isomers
† includes mixtures and individual emissions for butyl cellosolve

Table 2. Types of Thermal Oxidizers

Thermal Oxidizer Type	Relative Capital Cost	Operating Cost
Direct (TO) <i>No heat recovery – incineration</i>	Low Simple burner	Very High Continuous fuel feed required

Recuperative (RCO) <i>Heat recovered with exchangers</i>	Medium/High Complex air movement Complex heat exchange	Medium Large fuel use at start-up 70% heat recovery possible
Regenerative (RTO) <i>Reuse of reaction heat in retention bed</i>	High/Very High Large ceramic beds Complex air movement Complex heat exchange	Low/Medium Large fuel use at start-up Best economics for high organic pollutant loadings 95% heat recovery/reuse possible
Catalytic (CO) <i>Noble metal catalyst lowers burn temperature</i>	High/Very High Large ceramic beds Expensive noble metal catalysts	Medium Lower fuel use due to lower temp Can be combined with regeneration for effective fuel use Catalyst poisoning kills destruction efficiency

Background

As mentioned in the previous section, the destruction of organic pollutants (*e.g.*, VOCs) by oxidation into stable compounds requires the addition of energy for reaction initiation. The generic reaction can be written as shown in Equation 2:

All that varies between technologies is the method of energy application and how any unused energy is recovered for additional service.

Thermal Energy versus Electron Energy

Oxidation driven by heat is called thermal oxidation and a variety of commercial equipment is available for use by industry. These types of technology were summarized in Table 2. There are several advantages to thermal oxidation: 1) the chemistry is well known and predictable; 2) the technology is accepted by environmental agencies within the United States and overseas; and 3) there are many equipment suppliers who are experienced in air pollution control and who can fabricate custom solutions for each industrial application.

The most energy efficient configuration of thermal oxidation equipment is regenerative thermal oxidation (RTO), as the heat from the treated air is recycled back into the reaction chamber thereby optimizing energy reuse and overall energy efficiency.

However, there are disadvantages as well, most notably in the co-generation of CO₂ and with the tradeoff between initial capital cost/system complexity and on-going operating cost and maintenance. Thermal oxidation technology is dominated by the cost associated with the fuel that is used to generate the heat required to drive the oxidation process. Oxidation systems typically operate at temperatures greater than 1600°F and as high as 2200°F. Significant amounts of fuel are needed to heat the furnace to these temperatures and then maintain these temperatures throughout the work cycle. If the system is shut down at the end of the day, fuel must be burned at the start of the next day in order to bring the temperature back to minimum working levels. Regenerative thermal oxidizers use the heat generated by the burning VOCs to help generate heat and also use sophisticated heat exchangers to minimize heat losses. But these systems are only efficient at high organic loadings (>1% by volume) and when used continuously for many days at a time. Finally, the use of fossil fuels not only make thermal oxidizers expensive to operate, but it also leads to the generation of large volumes of CO₂, typically one to four orders of magnitude more than generated by the oxidation of the organic pollutants. Clearly, alternatives are required if greenhouse gas emissions are to be significantly reduced.

Electron beams (e-beams) are also capable of serving as the energy source that drives the oxidation of VOCs/o-HAPs to their combustion by-products. Commercial electron beam systems have been in use for nearly 50 years and AEB has been developing and manufacturing modular electron beam emitter subsystems for more than 10 years.⁹ Significant study into the detailed reaction mechanism for common organic compounds has been performed in laboratories equipped with very small scale, research grade electron beam systems. A sample of important literature references and key researchers in this field are shown in References 2 through 8. Detailed reaction pathways and chemical mechanisms for electron beam air treatment have been proposed. In general, the principal of electron beam initiated oxidation of organic compounds is straightforward:

1. electron energy is directly irradiated into the contaminated air stream

2. electrons scatter in the air, continuously losing their energy to the air and VOC molecules
3. chemistry occurs in the e-beam treated air, similar to the chemistry of atmospheric air plasmas

Electron induced oxidation differs from traditional thermal oxidation in important ways: 1) 100% of the energy in the electron beam is absorbed by the air, thereby causing the oxidation reaction to occur; 2) there are no warm-up and cool-down cycles, as the electron beams achieve stable operation in under one minute; 3) energy is only applied when VOCs are present and does not need to be maintained for any significant period of time before or after the polluted air stream is present; 4) fossil fuels are not directly employed, minimizing carbon dioxide production to only the molar quantities generated by the initial VOC/o-HAP; 5) simple systems designs and easy maintenance procedures yield very high up-time and minimal system maintenance.

Key parameters in electron beam oxidation are the initial energy of the electrons and their dose rate into air, as these determine the overall productivity of the system. The electron beam energy determines the maximum penetration distance into air; this in turn determines the size of the ducting that can be treated with electron beams. Figure 1 shows the theoretical depth distribution of absorbed energy into air for several initial electron beam voltages. Note that a 150kV electron beam travels more than 200mm in air; an electron beam accelerated to 175kV would travel nearly 300mm. By placing electron beams in a face-to-face configuration, complete and uniform electron beam treatment of an air stream can be ensured. Figure 2 shows the energy distribution when two 150kV electron beams are emitted into air from opposite directions; the optimum spacing to ensure complete air treatment is approximately eight inches. For this project two pairs of emitters in face-to-face configuration were used to research VOC destruction efficiencies.

As indicated above the other key parameter in electron beam oxidation of VOCs is the beam intensity or dose rate; the dose rate determines the overall rate of reaction, as electron beam oxidation requires a minimum dose to the air stream in order to ensure complete reaction occurs. In electron beam technology applications, dose is reported as the number of kiloGray (kGy) delivered to a material. Typical dose requirements for VOC/o-HAP oxidation by electrons are 5 to 15kGy.[4-7] For a fixed energy, increased dose is applied by increasing the electron current that is drawn from the filament and delivered through the emitter window.

The initial electron beam causes radical formation within the air ($\text{OH}\cdot$, $\text{O}\cdot$, etc.) and the organic pollutant. Active ozone (O_3) is also generated. Once radicals and ozone have formed, oxidation proceeds rapidly by the same chemical pathways as observed in thermal oxidation. The rate of oxidation is determined by the slowest step, typically formation of the initial radical within the organic compound.

Previous Experiments by AEB

We performed two early studies of VOC abatement in order to test the concept of using modular emitters for pollution control. A first generation air test system was capable of the following test conditions:

- two electron beam emitters operating at 100kV, 10mA (1kW) drawn power each
- maximum 200scfm of room temperature air flow (20-22°C, 25-50% RH)
- 50-100ppmv of VOC delivered by gravity- and nitrogen-fed nebulizer

The list of compounds studied, along with their target industrial applications, is shown in Table 3. The diagram of the test system is shown in Figure 3 and results are shown in Figure 4. The data were

consistent with prior published work²⁻⁸ and confirmed that it is important to characterize the electron beam oxidation for the family of compounds that will be used in the final application if absolute destruction efficiencies are to be determined. Note that, within a compound family, relative destruction efficiency (*i.e.*, ease of oxidation) increases with increasing molecular complexity. Also, compounds strong bond groups such as C=O (ketones, acetates) are more difficult to oxidize than compounds with groups that are easy to radicalize such as –OH (alcohols) or –O– (ethers).

AEB conducted additional experiments with the higher powered, second-generation air test unit. A single compound – Stoddard solvent, a mixture of aliphatic hydrocarbons similar to mineral spirits and important to the architectural coatings industry – was studied in more depth. Electron beam power, organic pollutant concentration and carrier air flow were all varied. Key findings were that the destruction efficiency of this single compound was independent of initial concentration over the range 10 to 1000ppmv. This is very promising, as real-world industrial processes rarely have stable emissions outflow with time. A concentration-independent process would be easier to engineer than one that required continuous measurement and feedback.

AEB Qualifications for Project

AEB has an experienced team of scientific, engineering, and program management professionals that could actively participate in the execution of this project; specifically, the principal investigator performed the early laboratory scale research studies and the both the principal investigator and the applications engineer manager have executed complex chemical projects in the past. Local universities could provide highly skilled undergraduate research assistants to execute the detailed program tasks. Support skills in finance, materials acquisition and equipment maintenance were already in place.

AEB's second generation Air Test Unit could be redesigned by in-house mechanical engineers and then modified to allow more flexible compound analysis. Electron beam emitters could be requisitioned from AEB's production line and a supply of appropriate specialty power supplies was available for purchase in a timely manner to support the project schedule. The factory laboratory facilities could be easily upgraded to allow safe testing. All of these resources enabled AEB to be uniquely qualified to execute a research program to provide the crucial data to allow this new technology to be implemented, with the resulting savings in energy, greenhouse gas emissions and business expense.

Statement of Project Objectives (SOP)

The objectives of this research project are to investigate and quantify the ability of direct electron beam destruction of volatile organic compounds and organic hazardous air pollutants in model industrial waste streams and to calculate the energy savings that would be realized by the widespread adoption of the technology over traditional methods. Specifically, this research will determine the quantity of electron beam dose required to remove the top 10 to 20 air pollutants from waste streams and provide the detail need to build a technical and economic model for the implementation of the technology in key industries including petroleum refining, organic & solvent chemical production, food & beverage production, and forest & paper products manufacturing.

Task 1 Application Model & Final Experiment Design – Model discussed in Benefits Assessment

Subtask 1.1 Literature Search and Application Model Construction

Subtask 1.2 Experiment Design and Documentation

Task 2 Potential Benefits Assessment – see Benefits Assessment

Task 3 Preparation of Test Equipment and Laboratory Facility – see Project Results

Subtask 3.1 Design and document modifications to Air Test Unit

Subtask 3.2 Manufacture modifications to Air Test Unit

- Subtask 3.3*   *Install and test Air Test Unit*
Subtask 3.4   *Acquire, install and test analytical equipment*
Task 4   *VOC and o-HAP Destruction Testing – see Project Results*
Subtask 4.1   *Development & testing of experimental protocols*
Subtask 4.2   *Testing of all documented VOC/o-HAP compounds as identified in Task 1*
Subtask 4.3   *Summary data analysis and report documentation*
Task 5   *Project Management and Reporting – no additional discussion beyond this report*
-

Table 3. List of chemicals studied in previous experiments

Industry	Compounds Studied		
Inks & Coatings	toluene	n-hexane	Stoddard solvent
	ethyl acetate	isobutyl acetate	
	methyl isobutyl ketone		
	ethanol	n-butanol	2-butoxy ethanol
Adhesives	xylene	dioxane	
Polystyrene	Styrene		
Semiconductor	isopropanol	propylene glycol methyl ether acetate	

Figure 1. Distribution of electron beam energy (dose) into air

Figure 2. Distribution of dose for two electron beams irradiating across an air gap

Figure 3. Configuration of initial laboratory experiments

Figure 4. Relative ease of destruction of compounds from initial laboratory experiments

Project Results

The primary technical results of this project were achieved during execution of Tasks 3 and 4 of the Statement of Project Objectives. These results are discussed below.

Air Treatment Unit System: Construction & Characterization (Task 3)

Key to the successful execution and interpretation of the VOC/o-HAP destruction tests was knowledge of the distribution of dose across the reaction zone. The dose delivered into the moving air stream under electron beam irradiation is governed by the KIDS equation:

$$\text{Equation 3} \quad D \text{ (kGy)} = K \text{ (kGy.ft/min/mA)} * I \text{ (mA)} / S \text{ (ft/min)}$$

D is the dose delivered to the moving air stream; K is a system constant depending upon the configuration of the electron beams and their operating accelerating voltage; I is the measured vacuum side drawn beam current and S is the speed of the air moving through the electron beam reaction zone. It is not possible to measure dose in real-time so the system constant, K , is calculated from dose data acquired under known conditions of I and S .

The first part of this project was the assembly and characterization of a modified electron beam system that would be able to provide flexible delivery of dose to a moving air stream. Our prior laboratory studies implied that the air flow within the second generation Air Test Unit (ATU) was not uniform and therefore did not allow sufficient exposure of the air flow to the electron energy. Also, the electron beam emitters that were installed did not provide adequate electron energy to the reaction zone to ensure all compounds could be studied. This task therefore focused on three activities: 1) modifying the air flow through the reaction zone to improve uniformity; 2) redesigning the reaction chamber to enable installation of higher power electron beam emitters; and 3) characterizing the air flow and electron beam profile to provide a map of dose across the reaction zone.

Figures 5a and 5b shows the results of finite element analysis of air flow through the ATU reaction zone before and after modifications were made to the input and exit air ducts, respectively. The primary modification was the addition of baffles on the flow out side of the reaction chamber. These baffles caused the air which was preferentially flowing past the far side of the reaction zone to be redirected towards center. Figure 6 shows air speed mapping across the zone at one air flow and confirms that the changes have improved the uniformity to better than $\pm 10\%$ minimum-to-maximum.

Due to the design of the radiation safety systems on the ATU it was not possible to make *in situ* measurements of electron energy across the reaction zone. Therefore the ATU electron beam configuration was simulated in a standalone test fixture (Figure 7a). Figure 7b is an image of the characteristic light emission that occurs when electron beams irradiate air and shows that the electron dose completely crosses the reaction zone. Dose measurement film was sent into the reaction zone at known distances across the air gap and specified velocity so that the electron dose profile could be determined.

Figure 8 shows the dose map across the reaction chamber air gap for maximum dose rate conditions for the four electron beam emitters. Knowledge of the beam current, I , and dosimetry tag speed, S , used to acquire these data allow us to convert these data to the dose delivered to a moving air stream under any combination of air speed and beam current. Note that there is a significant maximum-to-minimum dose uniformity ratio. This can be designed out of a full scale pilot system based on the data acquired in this phase of testing. However, without a major redesign and rework of the Air Test Unit it is not possible to make the dose more uniform. Practically speaking this non-uniformity causes a variation in the distribution of destruction across the reaction zone in these experiments; *i.e.*, some areas will achieve

higher destruction than others under the same electron beam and air flow conditions. However, gas analysis is performed on a sample that is an average composition of the air stream after treatment by electron beam oxidation. Also, it is not possible to assign a single dose value to the net average destruction that is measured for each set of conditions. In order to extract the dose that would be required to achieve the target destruction under uniform dose conditions we needed to build a model for interpreting these project results. This model was constructed and is discussed below.

VOC/o-HAP Delivery Methods Development (Task 4)

Primary Method: Nebulization with Pump Feed. Industrial waste air streams have VOCs and o-HAPs present in the gas phase. An important part of this task was the development and characterization of methods to transform the target compounds from their room temperature liquid or solid phase into the vapor phase more characteristic of an active waste stream. Based on prior laboratory experience we chose nebulization as the primary vaporization method. The advantage of this technique is that fine mist nebulizers are commonly available from analytical equipment suppliers as they are the method of choice for producing vapor samples in inductively coupled plasma mass spectrometry (ICP-MS) systems. For this project the nebulizer feed gas was high purity nitrogen (>99.99% assay) from pressure regulated cylinders. Liquid solvents were pumped into the nebulizer feed line initially using a peristaltic pump as this provided the most flexibility and repeatability in solvent delivery. Mass feed could be measured in real time by monitoring the mass of solvent in the feed container using a digital electronic scale. Solvent delivery repeatability was better than $\pm 5\%$ (1 standard deviation) for most compounds over one hour of experimentation time and often better than $\pm 2\%$. Figures 9 and 10 show the overall experimental set-up with ATU, VOC delivery systems and analytical equipment.

Optional Nebulizer Feed: Gravity. Additional variations of solvent delivery were developed to allow improved experiment performance for specific solvent systems. Low viscosity solvents such as acetone and methanol demonstrated the degraded mass feed repeatability with the peristaltic pump system as the pump speed had to be set to the lowest rate and pulsing occurred. This pulsing caused low frequency variations in the delivery of the concentration of VOC measured in the untreated air stream and the corresponding uncertainty in the destruction after electron beam oxidation. To allow these solvents to be studied with more repeatable and reproducible results a gravity feed apparatus was constructed for the nebulizer feed line. The apparatus consisted of a one liter separatory funnel mounted 2.5 meters above the nebulizer. The separatory funnel was filled with solvent, weighed and the level noted; starting mass was typically greater than 500g. When the level drop indicated that more than 10g of solvent had been delivered a known mass of solvent was added to the funnel. This ensured that the same net mass was being applied to the gravity feed and resulted in mass delivery repeatability of better than $\pm 5\%$ for these compounds.

Special Delivery Method: Direct Evaporation. Very high viscosity liquids such as tert-butanol and solids such as naphthalene provided additional challenges as they could not be delivered by nebulization in their neat forms. Dilution in an appropriate solvent was attempted but the presence of an additional compound in the air stream did not allow simple interpretation of the destruction data. In order to study these compounds a third apparatus employing direct evaporation was developed. A large Petri dish was loaded with the target compound, weighed and heated on a simple hot plate to approximately 50% of the boiling point. VOC feed rate was calculated by measuring the mass loss during a fixed time period. This was the most cumbersome and least repeatable method as the evaporation rate was dependent upon the changing mass of compound, the stability of the temperature provided by the hot plate. However, it did enable these compounds to be studied.

Analytical Methods

Air Sampling. In order to determine the concentration of the target VOC before and after electron beam oxidation samples of air need to be collected and fed into analytical instrumentation. We employed 0.7 liter Tedlar® air sampling bags from SKC, Inc. (Eighty Four, Pennsylvania); the bags were manually filled using an SKC Vac-U-Tube™ acrylic air syringe. Each bag was purged twice with nitrogen prior to filling. The sampling port was located two meters downstream from the exit of the ATU in order to ensure that adequate mixing of the air stream had occurred. Bags were sealed and then analyzed within one hour to ensure sample integrity.

Air Composition Analysis. The accepted method for determining the composition of species in waste air streams in research studies is gas chromatography with tandem mass spectrometry (GC/MS). The gas chromatography separates the air into its different constituents using a specially constructed resin columns. The separated effluent is then fed into the mass spectrometer for species identification. After careful evaluation of all commercial equipment options we selected Perkin-Elmer Clarus 600 GC/MS. A special air sampling system was installed on the GC to allow direct injection from the Tedlar sample bags into a purging loop; once the input line was purged with the sample gas it was automatically injected into the GC column using high purity helium. Identification of all initial VOCs and by-products was determined using matching to the NIST mass spectrometry database. At least three separate analyses were performed from each sample bag. Each VOC/o-HAP required separate experimentation to determine the proper temperature sequences for the GC/MS analysis. Purging experiments were also performed to ensure that the GC column produced no detectible organic compounds after each sample run.

Experimental Protocols (Task 4)

The majority of the work in the early months of this project was the establishment of an experimental protocol that would allow the generation of accurate VOC/o-HAP destruction data. The detailed experimental protocol has been documented and is available as a supplement to this report. There were 6 basic steps in the execution of the experiment protocol:

- 1) Establish stable air flow through the air treatment system
- 2) Begin injection of the target VOC/o-HAP and determine mass flow rate and net VOC/o-HAP concentration
- 3) Sample the air flow without electron beam oxidation treatment
- 4) Turn on the electron beam treatment system to the target total beam current conditions as indicated in the experiment matrix
- 5) Re-sample the air flow after electron beam oxidation treatment
- 6) Examine the composition of the air samples for change in initial VOC/o-HAP concentration and the formation of any by-products.

All data used in the final execution of project was performed at a single air flow, 250scfm and corresponds to average speed of 350ft/min through the reaction zone. Dose was varied by changing the total current introduced into the reaction zone from the four electron beam emitters. For most VOC/o-HAP experiments the electron beam conditions were those documented in Table 4.

Data Analysis

Each destruction experiment resulted in the calculation of % reduction of initial VOC/o-HAP concentration based on a ratio of peak areas between for the treated and untreated air samples. By-products were also identified and their relative concentration expressed as a percentage of the originating

VOC peak intensity.

Each VOC/o-HAP was then analyzed using the Linear First Order Model (Appendix) to determine the best estimate of uniform dose required to achieve greater than 90% destruction and the quality of the fit to the model. Figures 11 and 12 show Linear First Order Model plots for pine turpentine and benzene, respectively. The Linear First Order Model fits data from pine turpentine very well and estimates that 2-3kGy of dose is adequate to achieve target destruction. However, the model does not fit well to the behavior for benzene at higher dose rates. We believe that this is due to the presence of recombination reactions that can occur for compounds with high natural stability. There was insufficient time during this project to develop a more complex data interpretation model so the best and conservative fit to the model was used for all compounds.

Dose-Destruction Results

The selection of compounds studied in this work was based on their prominence in the domestic industrial emissions listing of non-halogenated compounds as documented earlier in Table 1. They are indicated in that table by an * symbol located next to the compound name. Nine compounds from the list representing more than 75% of non-halogenated VOC/o-HAP emissions were studied along with an additional six compounds that allowed a more complete family of materials to be examined. This work was the primary focus for six months of this project.

It should be noted that halogenated compounds could not be attempted in this project for safety reasons: these compounds are known to produce mineral acids as a product of oxidation (thermal or electron beam) and a special acid scrubbing system is required for their safe emission into the atmosphere. Such an acid scrubber was not available for this work.

Table 5 summarizes the results of the more than 100 experiments performed as part of this project. VOC/o-HAPs have been grouped by their chemical families: aliphatic hydrocarbons; aromatic hydrocarbons; alcohols; ketones; and other important solvents. The following observations can be made:

- 1) Aliphatic hydrocarbons require less electron beam dose than aromatic hydrocarbons with similar carbon units. This is expected due to the stability of the benzene ring towards primary ionization and radical formation; its resonance structure is likely to reform after ionization and therefore not have available low energy reaction sites for oxidation.
- 2) Within a chemical family, longer chains and more complex branching result in lower electron beam dose requirements. Mineral spirits are primarily straight chained hydrocarbons while pine turpentine contains more cyclic compounds. The more complex cyclic structure is more likely to ionize and less likely to recombine resulting in higher probability of successful oxidation.
- 3) Acetone is the primary byproduct formed during electron beam oxidation. While no longer considered by the EPA to be a VOC and therefore having unregulated emissions, it is preferred to have complete organic removal from the waste stream. This can be achieved but with high energy requirements.
- 4) Compounds with stable sub-groups are likely to have more complex reaction chemistry that will not directly follow the Linear First Order Model.
- 5) Most compounds can be removed from waste air streams to greater than 90% by the application of 10-15kGy. Additional work on a system with more uniform dose delivery and therefore more simple data interpretation is required to establish a definitive target value for universal solvent oxidation.

Summary

All VOCs/o-HAPs in this study could be treated using electron beam oxidation. As with other methods of oxidation, the amount of energy (*i.e.*, dose) required to achieve target destruction depends upon the chemical structure of the compound. Many compounds follow a linear, first order chemical reaction; compounds with stable structures such as aromatic rings and carbonyl groups may follow a higher order reaction sequence.

Figure 5. Finite element flow model output of the ATU showing improved flow: a) before modifications; b) after modifications

Figure 6. Air speed map across the reaction zone for three different volume flows

Figure 7. a) Configuration of electron beams in simulation set-up; b) visible light emission indicating electron dose across reaction zone

Figure 8. Dose Map across the reaction chamber air flow zone

Figure 9. Project equipment configuration: ATU & nebulizer with pump

Figure 10. Project equipment configuration: nebulizer & analytical equipment

Figure 11. Linear First Order Model applied to data from pine turpentine

Figure 12. Linear First Order Model applied to data from benzene

Table 4. Electron beam and air flow conditions for VOC/o-HAP experiments

Beam Voltage: 150kV (fixed)	
Air Speed: 250scfm	

I (mA) <i>Single electron beam emitter</i>	0	0.25	0.50	1.0	3.0	5.0	10.0	15.0	20.0	25.0
I_{tot} (mA) <i>Four electron beam emitter total</i>	0	1.0	2.0	4.0	12.0	20.0	40.0	60.0	80.0	100.0

Table 5. Summary of dose required to achieve >90% destruction of VOCs/o-HAPs

VOC/o-HAP	VOC Introduction Method	Linear FO Model Estimated Target Dose	Follow Linear Model?	By-Products
mineral spirits	Nebulizer	10kGy	Yes	acetone (15%) butanone (5%)
pine turpentine	Nebulizer	2-3kGy	Yes	None
benzene	Vaporization	>30kGy	No	acetone (5%)
toluene <i>methylbenzene</i>	Nebulizer	10-15kGy	Unclear	None
o-Xylene <i>1,2-bimethylbenzene</i>	Nebulizer	7kGy	Unclear	2,3-butanedione (trace)
Styrene <i>ethenylbenzene</i>	Nebulizer	2-3kGy	Yes	None
ethyl benzene	Nebulizer	10-15kGy	Unclear	None
naphthalene <i>bicyclo[4.4.0]deca-1,3,5,7,9-pentene</i>	Vaporization <i>could not maintain adequate volume</i>	n/a	n/a	-----
methanol	Vaporization	10-20kGy	Unclear	methyl nitrate (<5%)
ethanol	Vaporization	4-kGy	Yes	methanol (2%) methyl nitrate (10%)
isopropanol <i>2-propanol</i>	Nebulization	7kGy	Yes	acetone (40%)
n-butanol <i>1-butanol</i>	Nebulization	3-4kGy	Yes	butanal (1%)
sec-butanol <i>2-butanol</i>	Nebulization	3-4kGy	Yes	butanone (trace)
tert-butanol <i>2-methyl-2-propanol</i>	Vaporization <i>could only achieve 10ppm</i>	>30kGy	No	acetone (40%)
acetone <i>2-propanone</i>	Vaporization	>30kGy	No	None
methyl isobutyl ketone <i>2-butanone</i>	Nebulization	10kGy	Yes	acetone (40%) Other ketones (5%) Others (<<1%)
butylcellosolve <i>2-butoxyethanol</i>	Nebulization	3-4kGy	Yes	butyl formate (10%) n-butanol (5%)
ethylene glycol <i>1,2-ethanediol</i>	Nebulization <i>1:1 dilution with ethanol</i>	n/a	n/a	-----

Benefits Assessment

Analysis Strategy

Three types of potential benefits were evaluated for the use of direct electron oxidation versus thermal oxidation: 1) energy use reduction; 2) total operating expense savings; and 3) net CO₂ emission reduction, both in the current and future low carbon foot print electricity generation environments. The following strategy was taken to assess the potential benefits:

- A. Determine the amount of energy required to eliminate VOCs and o-HAPs using the results of this research project
- B. Build a model for the design of an electron beam pollution abatement system
  1. Total energy required based on the volume flow of air to be treated and the typical composition of the VOCs and o-HAPs to be treated;
  2. Capital cost based on number of electron beams required for the application and the support structure required to house the electron beams and move air safely in and out of the treatment zone
- C. Estimate the capital cost and energy use of the most energy efficient thermal oxidizer system, regenerative thermal oxidizers, from available industry information
- D. Compare energy use and costs for common end user profiles
- E. Project global benefits to adoption of direct electron beam oxidization using industry projections for the pollution control market

Details of the steps A through C are provided in Appendix “Cost and Benefits Models” and are based on the technical results of this project and interviews with members of the pollution abatement community. The actual cost savings are strongly dependent upon the prices for natural gas and electricity; EIA published numbers for June 2011 of \$5.06/MMBtu and \$0.0714/kWh were used for the model results discussed below.

The end user profiles for the specific benefits comparison were developed out of previous interviews with end users who are impacted by EPA regulations yet struggle with the economics of traditional pollution abatement system implementation. A profile for a traditional industrial manufacturer who has implemented traditional pollution abatement was also considered. These end user profiles are labeled and described as follows:

1. Local Small Producer. These small producers typically supply products and services to the consumer market in an on-demand basis using a retail service hour structure. Examples of these end users are body shops, small or custom graphics houses, decorative artists, and community bakers. They emit VOCs below the current emissions regulations but are vulnerable to proposed future regulations and cannot afford the initial capital expense and on-going operation and maintenance of a traditional RTO system. They usually do not have proper maintenance staff to keep a complex RTO system operating at maximum energy efficiency.
2. Regional Medium Source. These VOC/o-HAP emitters provide services to other companies in a non-retail, but non-continuous environment. The most common examples are regional dry cleaners, architectural wood primers, and commercial bakers. They often operate close to or above the current emissions regulations and either are forced to adopt pollution control technology or stop operation when monthly limits are reached. Because they do not operate in a continuous mode these installations experience higher net energy costs in order to maintain RTO temperatures during production idle time.
3. Batch Producer. Many industrial processes are produced in batch not continuous modes.

Examples include pharmaceutical pill coaters, ceramic kilns and metal panel coaters. These processes produce moderate volumes of VOCs/o-HAPs but occur in small to medium air flows over short (sub-shift, *i.e.*, 2-4 hour) intervals. The organic emissions must be abated but use of a continuous abatement process is energy inefficient and costly.

4. Continuous Producer – small volume. These producers have multiple, often identical, process lines that each produces a small volume of contaminated air. Examples of these producers include semiconductor fabs, food container producers (especially two and three piece metal can producers), coated web fabric and metal producers, and modular petroleum refiners. The total flow within the production facility may be large when all models are functioning but highly variable based on production schedules. Also, the physical locations of these lines may change and changing connections to a large central abatement system can be costly and often impossible to achieve.
5. Continuous Producer – large volume. These large regional producers of organic pollutants were targeted by the EPA for abatement with the initiation of the Clean Air Act. Examples include large chemical companies, wood processors, and food producers. The large air flows, static installations and continuous operation are ideally suited for traditional pollution control technologies.

Energy, Environment and Cost Benefits

Table 6 shows example end user pollution profiles and the resulting difference in energy use, energy cost, operating cost and carbon dioxide emissions using the models described in the Appendix. Note the obvious benefits in energy use and all costs for users that do not operate in a continuous mode, as energy is only expended when production is occurring and is not required to maintain the RTO temperature in idle time.

The total energy, environmental, and economic benefit of the adoption of EBO versus traditional TO can be sized by examining projected pollution abatement equipment sales and apply a conservative EBO adoption rate. The results of the model and the resulting energy and carbon dioxide savings projections are shown in Table 7 below. Details of the adoption model are provided in the Appendix. Key conclusions:

Energy. Even with this conservative estimate of adoption of the annual savings in energy use at the end of the 10 year initial adoption period is greater than 1 billion Btu. The cumulative estimated savings during this period is nearly 4 trillion Btu.

Environmental. There is a correlated savings in greenhouse gas emissions. Adoption of electron beam technology would result in a cumulative initial 10 year savings of more than 100,000 metric tonnes of CO₂. Note that in many user profiles greenhouse gas reductions of greater than 75% would be achieved.

Economic. An economic benefit to domestic industry is the reduction in system operation cost for electron beam air treatment vs. traditional thermal oxidation. The conservative estimate of cumulative savings to industry over the initial 10 year adoption period will exceed \$44 million. These savings can be used to retain jobs, encourage innovation and increase the profitability of impacted industries.

Other Benefits

The positive impact that adoption of electron beam air treatment on job retention and factory expansion would be significant. High population areas of the United States such as EPA Regions 1 - 3

(New England, New York and the Mid-Atlantic States), Region 5 (Upper Midwest), Region 7 (Texas) and Region 9 (California) are experience tight caps on VOC emissions for ground level ozone control. The availability of new, lower cost VOC abatement technologies will enable EPA to implement key aspects of the Clean Air Act without driving jobs and businesses out of these high population areas and potentially out of the country.

Table 6. Comparison of Energy Use, Costs and CO₂ Production between RTO & EBO

	Description	Production Profile		Difference: RTO – EBO				
				Energy		Operating	CO ₂	
		h/yr	scfm	MMBtu/yr	k\$/yr	k\$/yr	T, today+	T, green++
1	Local Small Producer <i>Body shop, small print shop, decorative arts studio</i>	3120	500	388 90%	1.2 58%	12.5 36%	15 66%	19 83%
2	Regional Medium Producer <i>Dry cleaner, architectural coater, small factory</i>	4800	2000	1458 84%	3.1 35%	16.6 38%	45 48%	69 74%
3	Large or Small Batch Producer <i>Pharmaceuticals, High tech manufacturer, university laboratory</i>	1000	1000	836 97%	3.8 87%	15.8 42%	42 89%	44 95%
4	Large Continuous Producer: small volume <i>Semiconductor fab, oil refinery module</i>	8000	2500	1598 74%	-0.8 -8%	13.4 29%	16 14%	66 57%
5	Large Continuous Producer: high volume <i>Chemical factory, wood producer</i>	8000	50000	31969 74%	-16.6 -8%	-177.0 -54%	315 14%	1325 57%

★ Assume 54.01kg/MMBtu natural gas and 0.61235kg/kWh. Source: DOE

★ Assume 50% reduction in electricity CO₂ emission (0.3062kg/kWh) by use of non-fossil fuel sources for electricity.

Table 7. Conservative projection of domestic benefits of EBO adoption through 2022

	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	Total
VOC Systems Sold	381	406	432	460	490	522	556	592	631	672	716	5858
EB Adoption Rate	0%	2%	5%	5%	10%	10%	15%	15%	20%	20%	25%	13%
EBO Systems Sold	0	8	21	23	49	52	83	88	126	134	179	763
Energy Savings	0	11668	42295	75839	147303	223143	344194	472537	656302	851734	1112797	3937812

MMBtu, \$	\$0	25	90	161	313	474	731	1004	1394	1809	2364	\$8365
CO ₂ Savings (tonnes)	0	359	1303	2336	4537	6872	10601	14553	20213	26232	34272	121278
Operating Savings, k\$	\$0	133	482	864	1677	2541	3919	5381	7473	9699	12671	44840

Commercialization

There will be several steps required to realize widely accepted commercialization of electron beam oxidation, addressing both the marketing and engineering of the technology.

Market & Applications Development

In the adoption of any new technology potential end users will want to demonstrate that their applications can be supported. All, government regulatory agencies such as the EPA and local enforcers such as state and local DEPs will require test data.

1) construction of a standard applications test system with uniform air flow and support facilities capable of safely handling the full range of industrial VOCs and o-HAPs including halogenated compounds and air flow regimes up to 2000scfm. This will enable final design of item 2) below and allow first stage applications validation to occur in a laboratory setting.

2) design, construction and assembly of a portable pilot scale system capable of being temporarily installed at a variety of industrially settings to allow demonstration and validation of the technology for VOC/o-HAP control up to 5000. This will generate the data required by end users and regulators to ensure rapid adoption and approval of new installations.

3) establishing partnership with one or more pollution abatement equipment manufacturers for the incorporation of EBO technology into an integrated pollution control and monitor system.

Engineering Development

It was discovered during the course of this research it is essential that the reaction chamber to deliver the most uniform electron dose across the air gap for maximum energy use efficiency. Also, the dose delivery is optimized when the air speed is lower, resulting in higher I/S values at the same net energy usage. Also, since initial capital cost is a strong factor in the adoption of any new technology and in ensuring key operating cost benefits, cost reduction activities must also occur. Therefore, key engineering activities for commercialization are therefore:

- 1) Development of an electron beam emitter system with higher accelerating voltage and wider beam width to increase the face area of the reaction zone and therefore reduce the speed of the air during EBO treatment. We are targeting 175kV of accelerating voltage and 24 inches of beam width, resulting in a greater than two times increase in reaction zone area and a corresponding reduction in air speed.
- 2) Reduction in the cost of manufacturing of the electron beam emitter system by 50% through re-engineering of the manufacturing process and reduced materials expenses.

AEB Commercialization Plans

Due to changes in internal business strategies and priorities, delays in implementation of critical VOC controls regulations by the EPA, recent reductions in the cost of natural gas, and the overall deceleration of the domestic and world-wide economy, AEB has elected to not aggressively pursue the commercialization of electron beam oxidation. However, as market, economic, and regulatory forces return to their expected directions in the coming 12 to 36 months this decision will be revisited and commercialization will be pursued.

Accomplishments

General

The objectives of this research program were to investigate and quantify the ability of direct electron beam destruction of volatile organic compounds and organic hazardous air pollutants in model industrial waste streams and to calculate the energy savings that would be realized by the widespread adoption of the technology over traditional methods. All tasks and milestones documented in the Statement of Program Objectives were completed. Specifically:

- Milestone 1: Applications model, economic and environmental benefit models and complete experiment plan completed.
  - Results are reported in the Benefits Assessment section of this document. Electron beam oxidation was shown to provide energy, environmental and economic benefits over current energy intensive thermal oxidation technology.
- Milestone 2: All equipment installed, tested and ready for use in completed laboratory facility.
  - A fully functional and practical experimental test set-up was completed.
- Milestone 3: All VOC and o-HAP testing completed, summarized and reported
  - Experimental methods were developed and documented. Fourteen industrially relevant VOCs and o-HAPS representing more than 80% of all industrial emissions in the United States were evaluated and documented

Publications

The principal investigator made an oral presentation on this project work in the session on “Emerging Applications” at the International Meeting on Radiation Processing, IMRP 2011, in Montreal, Canada on June 14, 2011. The title of the paper was “Electron Induced Destruction of Organic Air Pollutants in Active Waste Air Streams” and was distributed as part of the project during a previous quarterly report. It should be noted that this work had the most discussion of any presentation in the “Emerging Applications” session and more than a dozen requests were made for copies of the slides.

Student Work

Three cooperative education student interns from the Chemical Engineering Department of Northeastern University (Boston, Massachusetts) completed all or part of their “Middler” year work in support of this project.

- 1) Matthew Pelletier. Matthew was dedicated to the project for his entire six month assignment. He characterized the ATU air flow performance, developed the nebulizer-based VOC introduction systems and air sampling methods, and developed all GC/MS data acquisition and analysis methods. He acquired the primary VOC destruction data for ten of the fourteen fully characterized solvents.
- 2) Brian Lejuene. Brian succeeded Matthew on the project and completed the final three months of work. He developed the evaporation method for VOC introduction and acquired the primary VOC destruction data for the final characterized solvents.
- 3) Danielle Pesko. Danielle’s primary work assignment was outside of this project. However, she designed and executed the experiments to characterize the delivered dose across the reaction zone using the customized test set-up.

Conclusions and Recommendations

Electron beam oxidation has been demonstrated to be an effective and energy efficient method of removing volatile organic compounds and organic hazardous air pollutants from model industrial waste streams. The initial target end users for adoption of this technology would be small to medium producers of VOC/o-HAP emissions that operate on a non-continuous basis. These producers have not yet been universally regulated due to the lack of a capital and energy efficient control technology; electron beam oxidation would allow environment improvements with the lowest economic and energy impact.

Future activity should focus on two primary areas:

- 1) Continuation of research into the most optimum methods for delivering electron beam dose to the waste air stream. This will simplify data interpretation and allow the most energy efficient implementation of electron beam oxidation.
- 2) Development of pilot scale electron beam oxidation systems for field implementation and technology validation by end users and government agencies.

References

- ¹ B. Brunekreef and S. Holgate. "Air pollution and health". The Lancet 360 (2002): 1233-1242.
- ² H. Paur and H. Maetzing. "Electron beam induced purification of dilute off gases from industrial processes and automobile tunnels". Radiation Physics and Chemistry 42 (1993): 719-722.
- ³ B. Penetrante, M. Hsiao, J. Bardsley, B. Merritt, G. Vogtlin and P. Wallman. "Electron beam and pulsed corona processing of volatile organic compounds in gas streams". Pure & Applied Chemistry 68.5 (1996): 1083-1087.
- ⁴ D-H Han, T. Stuchinskaya, Y-S Won, W-S Park, J-K Lim. "Oxidative decomposition of aromatic hydrocarbons by electron beam irradiation". Radiation Physics and Chemistry 67 (2003): 51-60.
- ⁵ K. Hirota, H. Sakai, M. Washio and T. Kojima. "Application of electron beams for the treatment of VOC streams". Industrial Engineering Chemical Research 43 (2004): 1185-1191.
- ⁶ A. Chmielewski, Y. Sun, S. Bulka and Z. Zimek. "Review on gaseous chlorinated organic pollutants electron beam treatment". Radiation Physics and Chemistry 76 (2007) 1795-1801.
- ⁷ A. Chmielewski. "Application of ionizing radiation to environment protection". Nukleonika 50 (2005): S17-S24.
- ⁸ A. Chmielewski, A. Ostapczuk, Z. Zimek, J. Licki and K. Kubica. "Reduction of VOCs in flue gas from coal combustion by electron beam treatment". Radiation Physics and Chemistry 63 (2002) 653-655.
- ⁹ K. Felis, T. Avnery and A. Berejka. "Innovative energy efficient low voltage electron beam emitters". Radiation Physics and Chemistry 63 (2002): 605-608.
- ¹⁰ "Natural Gas Pricing". U.S. Energy Information Administration web site. http://205.254.135.24/dnav/ng/ng_pri_sum_dcu_nus_m.htm.
- ¹¹ "Monthly Flash Estimates of Electric Power Data – June 2011". U.S. Energy Information Administration web site. <http://205.254.135.24/cneaf/electricity/epm/flash/flash.pdf>.
- ¹² "Carbon Dioxide Emissions from the Generation of Electric Power in the United States". July 2000. US Department of Energy, Washington, DC 20585 and Environmental Protection Agency, Washington DC 20460. <ftp://ftp.eia.doe.gov/environment/co2emiss00.pdf>
- ¹³ "Voluntary Reporting of Greenhouse Gases Program: Fuel Emission Coefficients". US. Energy Information Administration web site. <http://205.254.135.24/oiaf/1605/coefficients.html>, Table 1

Appendices

Cost and Energy Benefits Models

Applications Benefit Model

This benefits model was constructed to allow flexible analysis based on the production profile of the targeted end user.

- Input data. The model requires characterization of profile information from the end user:
  - Air flow. The energy required to destroy VOCs is highly dependent up on the flow of air through the abatement system. Values for end users profiles were obtained through past information interviews and internet research.
  - Number of production hours per year. Small producers work in partial day or week shifts while large operators shut down production only for annual maintenance work.
- Energy use models
  - Thermal oxidizers.
    - Energy use. Data was obtained from selected interviews with manufacturers of modern and energy efficient thermal oxidizers and industry consultants. Based on their input we only considered the requirements for RTO systems and the following industry rule-of-thumb was employed:
      - $\text{Annual Energy (Btu)} = 1.08 * \text{AirFlow (scfm)} * 100$
    - Capital cost. The same interviews provided specific examples of the cost of RTO systems based on the treated air flow. A linear least squares fit was performed and yielded the following capital equipment cost estimate:
      - $\text{Capital (k\$)} = 195.03 + 0.09 * \text{AirFlow (scfm)}$
  - Electron beam systems.
    - Energy use. The results of this research provided the required electron beam dose was used to calculate the amount of electron energy required for >95% destruction (operating energy). The total delivered beam current required to treat an air stream was calculated using the KIDS equation.
      - $\text{Annual Energy (kWh)} = V \text{ (kV)} * I \text{ (A)} * \text{Production (h)} / \text{Efficiency (\%)}$
      - Where *Efficiency* is the ability of the power supply to convert AC wall power to the DC power required by the electron beam system. These numbers are available from power supply manufacturers
    - $\text{Current (mA)} = \text{Dose (kGy)} * \text{AirSpeed (ft/min)} / K$
    - Where K is a energy delivery efficiency constant based on the electron beam emitters employed in the system expressed in kGy.ft/min/mA.
  - Capital cost. The total amount of beam current required by the air stream determines the number of electron beam emitter pairs that would be configured in a system. The total cost of these emitters was multiplied by 30% to cover the cost of radiation shielding and duct work to produce a system equivalent to an RTO.

- Energy costs. Standard data on energy costs for industrial natural gas and industrial electricity were obtained from June 2011 data available from the DOE Energy Information Administration (EIA).^{10,11}
- CO₂ emissions. Standard data on the CO₂ produced by natural gas (54.01kg/MMBtu) and today's electricity (1.35 pounds/kWh = 0.61235kg/kWh) were obtained from the most recent DOE EIA reports.^{12,13} A future electric grid that employed sufficient non-fossil fuel sources to reduce CO₂ emissions by 50% was assumed for the "Green" projections and is an arbitrary value.

An example calculation provided by a custom Excel spreadsheet is shown in Figure 14 below.

Figure 13. Example calculation of using Applications Benefits Model

Application				
Air Flow SCFM	Production Hours/Day	Production Days/Week	Production Weeks/Year	Total Production Hours/Year
1000	16	6	50	4800
Industrial Energy Costs				
US Average - Industrial Natural Gas (\$/MMBtu)	US Average - Industrial Electricity (\$/kWh)			
5.06	0.0714			
System Costs				
Thermal Oxidizer Initial Capital (k\$)	Electron Beam Initial Capital (k\$)	Thermal Oxidizer Annual Maintenance (k\$)	Electron Beam Annual Maintenance (k\$)	Years of Depreciation
202.1	130.0	20.2	13.0	15
Cost Model				
Thermal Oxidizer Operating Rate (Btu/h)	Thermal Oxidizer Energy/Production Hour (\$)	Electron Beam Power (kW)	Electron Beam Energy/Production Hour (\$)	Delta Savings TO-EB Energy/Production Hour (\$)
108000.0	0.91	8.2	0.59	0.32
Cost Comparison				
Thermal Oxidizer Annual Energy (k\$)	Electron Beam Annual Energy (k\$)	Thermal Oxidizer Total AOC (k\$)	Electron Beam Total AOC (k\$)	
4.37	2.82	38.0	24.5	
Delta Energy Savings TO-EB (k\$, %)		Delta AOC Savings TO-EB (\$, %)		
1.5		13.6		
Energy Comparison				
Thermal Oxidizer Annual Energy (MMBtu)	Electron Beam Annual Energy (kWh)	Electron Beam Annual Energy (MMBtu)		
864	39529	135		
Delta Energy Savings, TO-EB (MMBtu, %)		729		84%
CO2 Savings				
Thermal Oxidizer Annual CO2 (kg)	Electron Beam Annual CO2 - today (kg)	Electron Beam Annual CO2 - green (kg)		
46665	24206	12103		
Delta CO2 Savings Today, TO-EB (tonnes, %)		22		48%
Delta CO2 Savings Green, TO-EB (tonnes, %)		35		74%

Adoption Benefits Model

Given the wide range of end user profiles in domestic industries that require organic pollution abatement it is difficult to make an accurate assessment of technology adoption. In order to estimate the energy, environmental and economic benefit of electron beam abatement technology a conservative approach was taken. The following steps were employed:

1. Estimate the total number of domestic VOC/o-HAP pollution abatement systems sold using total market sales available for 2009 and applying an industry projected growth rate.
2. Select a single end user profile and calculate the energy, environment and economic savings using the Application Model discussed above.
3. Assign conservative adoption rates for each subject year.
4. Calculate the benefit in each year for new adoption of EBO technology.
5. Calculate the annual benefit of existing and new EBO technology installations.

For this calculation the Regional Medium Producer end user profile was selected. Estimated total market sales and average system prices for calendar year 2009 were used as a baseline for calculations. An annual growth rate of 6.6% was then applied. Results are shown in Figure 15 below.

Figure 14. Snapshot of Adoption Benefits Model

Electron Beam Benefit Assumptions		Reference Application	
EBO System Capital Cost	\$130,000	End User Profile	Regional Medium Producer
System Capital Cost Savings (RTO-EBO)	\$81,050	Air Volume Flow (scfm)	2000
CO2 savings/system, tonnes (RTO-EBO)	45	Production Hours/Year	4800
Energy savings/system, MMBtu (RTO-EBO)	1458		
Energy cost savings (RTO-EBO)	\$3,098		
Operating cost savings (RTO-EBO)	\$16,607		
Anchor Data: VOC Equipment 2009 Sales Estimates		Assumptions	
Total Market Size	\$158,000,000	Market Growth Rate	6.6%
Average System Price	\$500,000	Source: private conversations with industry experts	
Number of Systems Sold	316	2012 Sales Projections based on 2009 estimates	381
		Energy Costs (2011 values)	
		Natural Gas, /MMBtu	\$5.06
		Electricity, /kWh	\$0.0714

Opportunity	Calendar Year											Total
	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	
E-Beam System Adoption Rate	0%	2%	5%	5%	10%	10%	15%	15%	20%	20%	25%	
New VOC Systems: All Technologies	381	406	432	460	490	522	556	592	631	672	716	5858
New VOC Systems: EBO Only	0	8	21	23	49	52	83	88	126	134	179	763
Energy Savings: New EBO Systems (MMBtu)	0	11,668	30,627	33,544	71,464	75,839	121,051	128,344	183,765	195,432	261,062	1,112,797
Energy Savings: New & In-Service EBO Systems (MMBtu)	0	11,668	42,295	75,839	147,303	223,143	344,194	472,537	656,302	851,734	1,112,797	3,937,812
Greenhouse Gas Savings: New E-Beam Systems (tonnes CO ₂)	0	359	943	1,033	2,201	2,336	3,728	3,953	5,660	6,019	8,040	34,272
Greenhouse Gas Savings: New & In-Service EBO Systems (tonnes CO ₂)	0	359	1,303	2,336	4,537	6,872	10,601	14,553	20,213	26,232	34,272	121,278
Energy Cost Savings: New EBO Systems	\$0	\$24,784	\$65,058	\$71,254	\$151,802	\$161,096	\$257,134	\$272,624	\$390,348	\$415,132	\$554,542	\$2,363,774
Energy Cost Savings: New & In-Service EBO Systems	\$0	\$24,784	\$89,842	\$161,096	\$312,898	\$473,994	\$731,128	\$1,003,752	\$1,394,100	\$1,809,232	\$2,363,774	\$8,364,600
Operating Cost Savings: New EBO Systems	\$0	\$132,858	\$348,751	\$381,966	\$813,753	\$863,575	\$1,378,399	\$1,461,435	\$2,092,509	\$2,225,367	\$2,972,691	\$12,671,304
Operating Cost Savings: New & In-service EBO Systems	\$0	\$132,858	\$481,609	\$863,575	\$1,677,329	\$2,540,904	\$3,919,302	\$5,380,737	\$7,473,246	\$9,698,613	\$12,671,304	\$44,839,476

Data Compendium #1: Gas Chromatograms for all Compounds

The following figures show gas chromatograms for all compounds addressed during this work.

- Chromatograms labeled “Untreated”(various colors of text) were samples collected from air dosed with the target VOC/o-HAP but not subjected to electron beam oxidation.
- Chromatograms labeled “Treated” (also various colors of text) received the maximum possible electron beam power for our test system: four electron beam emitters each operating with an accelerating voltage of 150kV and drawing 25mA of vacuum-side beam current.
- For all data the air volume flow was controlled at 250scfm, corresponding to an average air speed of xxxx feet/min. This therefore corresponds to an I_{tot}/S ratio of YYYY.

Figure 15. GC/MS – mineral spirits

Figure 16. GC/MS – pine turpentine

Figure 17. GC/MS – benzene

Figure 18. GC/MS – toluene

Figure 19. GC/MS – o-xylene

Figure 20. GC/MS – ethyl benzene

Figure 21. GC/MS – styrene

Figure 22. GC/MS – naphthalene 1:1 in ethanol

Figure 23. GC/MS – methanol

Figure 24. GC/MS – ethanol

Figure 25. GC/MS – n-butanol

Figure 26. GC/MS – s-butanol

Figure 27. GC/MS – t-butanol

Figure 28. GC/MS – acetone

Figure 29. GC/MS – methyl isobutyl ketone

Figure 30. GC/MS – ethylene glycol 1:1 in ethanol

Figure 31. GC/MS – butyl cellosolve

Data Compendium #2: Gas Chromatography Retention Times and Mass Spectra of All By-Products

By-Product	Produced By	CG Retention Time (minutes)
Acetone	mineral spirits isopropanol t-butanol methyl isobutyl ketone benzene styrene ethyl benzene	4.8
Butanal	n-butanol	5.27
Methanol	ethanol n-butanol	5.37
Methyl nitrate	ethanol methanol t-butanol acetone	5.79
Butanone (MEK)	mineral spirits	6.28
Butyl formate	butyl cellosolve	6.57
Benzaldehyde	styrene	12.85

Figure 32. MS Identification of by-product – acetone

Figure 33. MS identification of by-product – butanal

Figure 34. MS identification of by-product – methanol

Figure 35. MS identification of by-product – methyl nitrate

Figure 36. MS identification of by-product – butanone (MEK)

Figure 37. MS identification of by-product – butyl formate

Figure 38. MS identification of by-product – benzaldehyde

Data Compendium #3: VOC removal versus treatment conditions with linear first order model overlay

Figure 39. Data & Model for Mineral Spirits

Figure 40. Data & Model for Pine Turpentine

Figure 41. Data & Model for Toluene

Figure 42. Data & Model for Ethyl Benzene

Figure 43. Data & Model for Benzene

Figure 44. Data & Model for o-Xylene

Figure 45. Data & Model for Styrene

Figure 46. Data & Model for Methanol

Figure 47. Data & Model for Ethanol

Figure 48. Data & Model for norm-, sec- and ter-Butanols

Figure 49. Data & Model for Acetone

Figure 50. Data & Model for Methyl isobutyl ketone

Figure 51. Data & Model for Butyl Cellosolve