Final Technical Report

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List of Acronyms

MPIC – microwave plasma isolation chamber
RF – radio frequency
MW - microwave
MAT – microwave assist technology
GC – gas chromatograph

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Executive Summary

The overall objective of this project titled “Microwave enhanced direct cracking of hydrocarbon feedstock for energy efficient production of ethylene and propylene” is to significantly decrease the energy consumed in the cracking of hydrocarbons through the application of direct microwave heating. Specific project goals were to demonstrate the viability of this method through 1) an extensive literature survey, 2) experimental laboratory testing, 3) cost benefit analysis, 4) collaborating with an industrial partner.

The benefits of microwave processing over conventional heating are obtained by either 1) direct heating of reaction gasses via a microwave plasma or 2) rapid heating of a thin carbon susceping layer which heats the reaction gasses. Heat transfer in the conventional method is limited to conduction through metal pipes. This indirect method of heating is energy intensive and inefficient. In addition, it leads to coking, which further decreases the efficiency by insulating the pipes and causing excessive maintenance downtime. The possibility of reducing coke formation through lower processing temperatures and elimination of metal tubing in the hot zone is a strong advantage of the microwave process. Furthermore, according to previous scientific studies for the plasma method, there is excellent potential for microwave processing to increase the yield and selectivity of ethylene and propylene, compared to conventional methods[1, 2]. Increased yield translates to more products with the same resource input, which is of great interest to the industry.

Initial conservative energy saving projections show that microwave processing could save 195 TrilBTU/yr in 2020, through the conversion of 10% of the ethylene production market (28.3 MM tons/yr). Taking into account the amount of energy required to produce one ton of ethylene (13.9 MMBTU/ton)[3] multiplied by 10% of the market (2.8 Mil tons/year) yields an energy usage of 3.9 Tril BTU/year. Ceralink is assuming a 50% energy savings based on converting to microwave processing, thus saving the industry 195 Tril BTU/year based on the converted market segment. The 10% market conversion would be roughly equivalent to 16 microwave based ethylene crackers with an average output of 150,000 tonnes/year. The reduced energy consumption also translates to a reduction in green house gas emissions. The burning of natural gas emits 117 lbs of CO₂ per 1 million BTU’s of fuel burned[4]. Reduction of carbon dioxide emissions based on reduced fuel consumption would yield a reduction of 22.8 Bil lbs of CO₂ in 2020. An additional benefit is that the conversion from gas fuel to electric makes the energy consumption easier to quantify.

Ceralink performed background work to understand the industry requirements for implementation of direct, localized microwave heating in the chemical industry. A microwave single-mode system with a plasma applicator was selected as the preferred method and a laboratory scale system was design, built and tested. A series of experiments were conducted which varied microwave power, system pressure, and gas flow rates to explore product output. A gas chromatograph was used to identify and quantify the product species, which included hydrogen, methane, acetylene, and ethylene. This initial work has proven this method to be feasible.

Results indicated that it was possible to crack ethane and obtain ethylene with high product conversion and high ethylene selectivity. The results of the gas chromatographic analysis for several different run parameters are presented. The yields from the microwave reactor (carbon susceptor) were consistent with results predicted by SPYRO[®] in a theoretical reactor operating under similar conditions of temperature and residence time. These initial results indicate there may be advantages of microwave heat transfer compared to conventional combustion furnaces. This may allow novel reactor designs that result in more efficient production of ethylene. Supplemental studies are needed to continue the laboratory testing and

refine processing parameters to explore ambient pressure processing and using steam as a dilution gas instead of argon.

It is recommended that this work be continued in order to further explore the microwave processing conditions with respect to flow rate, pressure, and microwave power. Considering scale-up, it would be advantageous to find operating conditions closer to ambient pressure, where good product conversion could still be maintained. It would also be beneficial to decrease or omit the argon carrier gas. Steam could be explored as a dilution medium, which is in line with current industry practice. A longer column for the gas chromatograph could be obtained to identify species heavier than ethane, for a more complete picture of the reaction kinetics, and a better comparison to the SPYRO[®] model.

The approach for commercialization of this technology will require continued research and development to prove out the merits of the process and refine the benefit projections. From this initial phase of project work, Ceralink and Technip have a joint development agreement in place. Ceralink will seek funding to continue this work from several sources. Ceralink and Technip have entered discussions on a follow-on project. If an agreement can be reached, Technip will provide research funding for continuation of work on the microwave cracking laboratory system modification for continuous flow ethane, data acquisition, and analysis. The follow-on project will likely include the design of a pilot scale prototype.

Introduction

Objectives of the proposed project were to perform early stage research needed to explore and define key technical concepts for highly energy efficient direct microwave heating in the chemical processing industry. The use of microwaves for the cracking of hydrocarbons was explored, to replace energy intensive indirect heating methods. A further objective was to explore engineering concepts for practical application of the direct microwave cracking technology as a seamless retrofit to current technology.

Ceralink Inc. (a female owned company specializing in commercializing energy efficient technologies), Rensselaer Polytechnic Institute (RPI), and Technip (a world leader in ethylene production and project management) collaborated to investigate the hydrocarbon-microwave interaction mechanisms, through modeling, and direct microwave experiments on the precursors and products of ethylene production. RPI has expertise in microwave modeling, including hydrocarbon feedstock, and developed a model specific to the microwave plasma heating process. In addition, Ceralink designed, built and performed laboratory heating studies using a microwave plasma reactor with ethane as the hydrocarbon feedstock. Ceralink engineers working with Technip partner engineers to design a retrofit concept for implementation of the microwave technology to an ethylene production system.

Ethylene was chosen for this concept definition study for the following three reasons. First, the cracking of hydrocarbon feedstock for the production of ethylene and its co-products is the single most energy intensive processing step in the chemical industry. Second, ethylene is one of the largest volume chemicals produced annually. Third, the breaking down of large hydrocarbons is needed for many chemical processes, including refining and waste conversion. The results from this microwave study have the potential to be transferable to these and other sectors of the chemical processing industry.

Direct microwave heating technology is expected to reduce the energy required for cracking by 50-75% to save 10-15% of the total energy used in the chemical processing industry; this savings is equivalent to nearly 600 Trillion BTU's annually. In addition, direct microwave heating of the hydrocarbons will reduce the temperature of the reactor skin, thereby reducing or eliminating coke build up on the reactor wall. This will improve the lifetime and efficiency of current crackers by minimizing down time. CO₂ emissions will be reduced by 35 million metric tons annually, primarily with the minimization of energy

consumption, and secondarily with the reduction of coke formation (as CO_2 is a major bi-product of the decoking process).

Background

The chemical industry is one of the most energy intensive industries in the United States [1]. The production of ethylene and propylene stands out as the most energy intensive processes as conventional heating methods (convection and radiant heating mechanisms) are found to be only 45% efficient in the hot zone of even the newest, most advanced facilities [1], see example in Figure 1. A large portion of the losses are due to heating non-product, such as the reactor walls. Through investigation, microwave energy has been identified as a method to directly heat the hydrocarbon feedstock for a large, sustained energy reduction impact.

Ethylene and other olefins are produced from hydrocarbon materials and dilution steam fed into furnaces that require large amounts of fuel. The fuel (usually in the form of natural gas) is burned to produce the temperatures required to drive the cracking reactions, usually in excess of 850°C . In the cracking furnace, the heat is transferred from the combustion products to the reactor coils via radiant and convective heat transfer, see schematic in Figure 2. Since this conventional heat transfer approach requires a substantial temperature driving force, less than half the energy released from the combustion of the fuel is actually transferred directly to the furnace coils that contain the hydrocarbons. The balance of the fired energy is recovered for feed preheating and steam production.

Conventional heating of hydrocarbon feedstock has several drawbacks. Through radiant heating, the reaction tubes are heated with burners located within the refractory lined reaction box. These tubes absorb the radiant heat, and then transfer it to the coking on the ID of the tubes before heating the feedstock material. Often it is observed in industry that the reaction is not completing and thus the temperature of the reactor box is raised to aid in the completion. The elevated tube temperature however increases the skin temperature of the reactor tube and promotes coke build up. Coke build up reduces the pressure within the reactor tube and decreases the performance of the reactor. Often the reactors are taken out of commission for decoking, which causes thermal wear on the reactor tube in heating and cooling reducing the reactor lifetime.

Figure 1. Digital photograph of an industrial ethane cracker.

Figure 2. Cross-sectional illustration of a conventional steam cracker (Notice the coke build-up on the ID of the reactor tube walls and the heat escaping the reactor box)

Another major energy sink is located at the exit of the reactor box. The hydrocarbon is indirectly heated via heat transfer from the reactor tube. This reactor tube exits the reactor box and takes a significant amount of energy with it. The hot tubes leaving the reactor box need to be quickly cooled to maximize yields. This cooling is also an energy intensive process which is essentially wasting a portion of the additional energy placed into the reaction box to overcome heat losses in the initial heating stage.

The use of microwave energy for direct heating of materials is quickly becoming a vital asset to many industrial processes because of its highly efficient energy transfer mechanisms. Microwave and radio frequency (RF) heating methods have already been proven useful and implemented successfully in drying processes, sintering of ceramic components, metal processing, and plasma formation[2-5]. Recent studies using microwave energy and plasma formation in materials processing have shown promising results in coal gasification, highly efficient combustion, and waste conversion [6-9].

Early stage work has been performed exploring microwave processing of hydrocarbons. Analysis of the literature involving microwave and plasma processing of hydrocarbon materials shows that cracking is often the observed reaction, indicating a strong affinity for this sort of reaction. Furthermore, when compared to the conventional methods of reaction, the microwave assisted runs are generally faster and achieve better outputs [10, 11]. The two following studies are good representations of this sort of behavior. Dominguez et al. demonstrated successful pyrolysis of sewage sludge using microwave radiation with char and graphite (materials similar to coke, a byproduct of ethylene production) as absorbers [12]. In addition they found that the microwave method had shorter processing times, higher percentages of the desired aliphatic product, and fewer environmentally harmful compounds. Ioffe et al. showed the ability to crack *n*-hexane using microwave radiation and achieved products similar to those found in high temperature conventional cracking [13]. The use of microwaves was shown to produce a high ethylene yield and much lower levels of coke formation when compared to conventional cracking. Xing et al. used a plasma processing technique to instantly generate lighter hydrocarbons to help reduce

exhaust gas agents [14]. Within the study *n*hexane was also processed in the same fashion and cracking was the only reaction observed. The results from these studies indicate good potential for microwave assisted cracking of hydrocarbon feedstock for ethylene and propylene production.

The hydrocarbon processing sector of the chemical industry is constantly trying to improve the efficiency of its processing techniques because of the massive amounts of energy consumed. Their efforts have been focused on maximizing the efficiency of an intrinsically inefficient process of indirect heating of hydrocarbons. Often new techniques are developed to continually adjust flow of the feedstock, temperature and, heat transfer among a variety of other variables. These minor adjustments have such a minimal impact on the process, the energy savings are negligible. In order to really address the energy intensity problem, a new method of processing needs to be developed which utilizes a direct hydrocarbon heating approach.

Direct localized microwave heating offers an innovative method of hydrocarbon cracking that has the potential to revolutionize the chemical industry. Attempts at using microwave and plasma processing of hydrocarbons have shown promising results, but until now, there has been no significant attempt to better understand the mechanisms and investigate the scalability of such technology.

Expertise in the analysis of microwave and materials interactions places our research team in a unique position to successfully implement test methods and practices aiding in the commercialization of hydrocarbon cracking using microwave technology. In conjunction with key research partners, we have characterized the interactions of a wide array of materials and used the knowledge gained to more efficiently heat, process, and treat the materials. Further, it has become standard practice for us to elevate our novel processing techniques into fully scalable industrial equipment. Our university partner has an extensive knowledge base in the modeling of microwave heating systems and has demonstrated the ability to maximize the efficiency of heating systems time and time again. This team has developed a strong understanding of the interactions between hydrocarbon feedstock and microwave plasma energy. This deep understanding is necessary groundwork for the development of a scalable technology that can change the future of hydrocarbon cracking.

Dr. Holly Shulman, founder and President of Ceralink, (PhD EPFL Switzerland, MS University of Pittsburgh, BS Alfred University) has 25 years of experience in ceramics and materials, with specializations in toughened ceramic processing, high temperature structural materials including Si₃N₄, SiC reinforced Al₂O₃, ZTA, and ZrO₂, calcining of barium titanate, pigments and phosphors, as well as cutting edge microwave process development. Dr. Shulman has extensive experience developing and licensing ceramic materials and process technology. Ms. Morgana Fall, Operations Engineer (B.S. Alfred University), has 9 years of experience in ceramic engineering and microwave materials interactions. Ms. Fall coordinates Ceralink's microwave equipment design work, and has designed several Microwave Assist Technology (MAT) kilns, from lab to production scale. Ms. Fall was responsible for the technology transfer for MAT when Ceralink licensed the technology in 2004. Ms. Fall has comprehensive knowledge of MAT process development and experimentation. Her ability to interpret microwave dielectric property data as it pertains to heating is a critical skill. Mr. Shawn Allan, Senior Materials Engineer (MS Georgia Tech), has 9 years of experience in ceramic and metals processing. Mr. Allan is an expert in microwave dielectric properties, and microwave process development for calcination reactions. Patricia Strickland, CEO of Ceralink (BA Alfred University), has over 15 years of experience in finance and business management. She has a strong background in strategic partnering and has been successful in negotiating joint venture and licensing agreements. Ms. Strickland has been with Ceralink since 2001.

Results and Discussion

The results and discussion are presented by task. The primary goals of this study were to:

- Establish feasibility of microwave hydrocarbon cracking
- Develop microwave hydrocarbon cracker design
- Model reactor and reactions
- Develop prototype design

Task 1. Investigation of Feedstock and Products

A comprehensive literature review was put together for the cracking of hydrocarbons, which included specifics on feedstocks and analysis of breakdown of hydrocarbons. Currently, the petroleum industry uses a combination of naphthas (alkanes), ethane and propane, LPG, natural gas, and gas-oil to produce ethylene (C_2H_4) and propylene (C_3H_6) via steam cracking. High molecular weight feedstocks result in products with greater yields of aromatic, carbonaceous, and heavy oil compounds whereas lower molecular weight feedstocks produce greater yields of light olefins such as ethylene and propylene, a difference explained by the greater activity of high weight hydrocarbons relative to light hydrocarbons. Through discussions with our industrial partner, it was determined that propane (C_3H_8) would be appropriate for modeling and laboratory scale experimentation and is relatable to industrial practice. Further research showed that ethane (C_2H_6), could be obtained, and this was a better choice, as ethane is used in industry as a feedstock and would compare more directly to the industry standard.

Three general methods are used in industry to produce ethylene and propylene: thermal (steam) cracking, fluid catalytic cracking (FCC), and oxy/dehydrogenation. The following information was gathered on steam cracking and fluid catalytic cracking.

Thermal (steam) cracking is a method which employs heat and/or pressure for hydrocarbon cracking. In steam cracking, a high temperature stream of steam is injected into the hydrocarbon feedstock stream. Steam cracking occurs in three stages: Pyrolysis (A), primary fractionation/compression (B), and product recovery/fractionation (C).

Fluid catalytic crackers combine a hot fluidized catalyst material, commonly a zeolite called faujasite with the feedstock stream. As feed contacts the zeolite, it is vaporized and is catalyzed, undergoing cracking as the mixture travels the reactor. The catalyst is then regenerated (removed of coke) and recycled.

A literature review was conducted to help select the best method to apply microwave energy. Based on these findings, we were able to focus on microwave plasma processing as a viable method. The paper by Mora et al was particularly interesting and is discussed below.

Mora et al[1], have produced a range of cracked products, most notably ethylene, by mixing pentane, hexane, and heptane gas into a microwave induced argon plasmas. Mora's group found that at high powers ($>300W$) and slower feed rates resulted in $\sim 80\%$ selectivity and $\sim 70\%$ conversion of cracked products to ethylene. In general flow rate and applied microwave power have significant influences on converted products, i.e. low applied power per unit of feed favors hydrogen whereas high power per unit of feed favors ethylene. Figure 3 graphically represents selectivity as a function of microwave power from Mora's results. This paper was discussed with Technip, who indicated that these results were very encouraging. They stated that selectivity greater than 60% and a conversion greater than 50-55% for ethylene would be a significant to the industry.

Figure 3. Graph of A) selectivity to ethylene (%) and B) selectivity to acetylene/hydrogen (%) as function of

One of the questions raised by Technip was whether or not a different mechanism existed which occurs during microwave plasma cracking vs. a conventional arc plasma process. Initial research on microwave processing indicates it is similar to thermal cracking, FCC, and dehydrogenation. Plasma cracking occurs via free radical mechanisms, i.e. high energy argon ions sever C-C and C-H bonds resulting in ions which continue to react until only stable particles remain. For example, the following represent possible reaction pathways of reaction for propane:

If a C-C bond is severed:

If a C-H bond is severed:

This concluded task 1 (one) of the project. A significant amount of information was gathered in this task in order to proceed with confidence in building and testing our lab-scale design.

Task 2. Explore Microwave Cracking Systems

This task built on the research from Task 1 and took a detailed look at the equipment used in hydrocarbon cracking. Ceralink's approach was to develop concept designs for 1) a retrofit of existing crackers and 2) design it as purpose built. The designs concepts were actually developed after the work in Task 3, where the results from the laboratory testing could be incorporated. The preliminary design for scaling up a microwave plasma reactor is shown in Figure 4. The final design is shown in Figure 5 and Figure 6.

It was determined that the purpose built and retrofit designs would be pretty similar. The microwave plasma would replace the hot furnace section in the existing crackers where metal tubes pass through a

gas flame heated chamber. An array of microwave surfaguides with quartz tube sections would serve as the “hot zone”, Figure 4. The current metal tubes would only need to be replaced in a small ~4 ft sections by quartz tube, where the tube passes through the microwave zone. Due to the simplified process, each 4 ft. section of quartz tube would replace a significantly larger length of metal tubes in the scaled up microwave plasma isolation chamber. Due to the inefficiency of the steam cracking method, multiple passes are necessary to ensure the maximum amount of hydrocarbon molecules in the feedstock are cracked. The gas molecules, due to the laminar flow of the fluid, are not mixed quickly enough in the residence time allotted for production of the desired olefins. Multiple passes and multiple tubes (which require even more heating) are required for assisting in the mixture of the gas by inducing turbulent flow. There is potential that the microwave process could effectively convert the hydrocarbon feedstock in a single pass and alleviate some of these issues.

Figure 4. Computer aided design drawing of the microwave plasma array for scale-up.

Figure 5. Design schematic for a retrofit microwave plasma isolation chamber. This would be a replacement for the pyrolysis chamber of the conventional cracker.

Figure 6. Design schematic for a purpose built microwave plasma isolation chamber.

The process of dehydrogenation and how microwave could be applicable was also investigated. Conventionally, dehydrogenation and oxydehydrogenation are two methods employed to promote

cracking of hydrocarbons in the presence of a catalyst, the latter also combining an oxidizing agent such as O_2 or CO_2 in gaseous form. High selectivity and high conversion rates have been achieved by a multitude of research groups, as reviewed by M.M. Bhasin et al[2], incorporating an impressive range of feasible catalyst materials. In industry, chromia-alumina combined with platinum/platinum modifiers are commonly used for dehydrogenation, whereas platinum and vanadium catalysts are commonly used for oxydehydrogenation. The catalyst and acid sites function by activating C-H bonds in paraffins, thereby cleaving them and forming free radicals which further decompose into the appropriate olefin.

It was determined that microwave heating could have some potential benefit to the dehydrogenation process, where the microwave energy would be used to heat a catalyst, which in turn strips the hydrogen atoms. Microwave energy could also be used to speed up the catalyst regeneration process, where the catalyst is heated.

Task 3. Select Microwave Compatible System

This Task, originally slated to begin on 1/26/11 started early to ensure sufficient time to acquire, set up lab equipment and perform testing. A laboratory scale microwave plasma cracking system (Figure 7) was designed and parts obtained from Gerling Applied Engineering. A LabVIEW program for controlling the system was developed and gas handling systems, including mass flow controllers, were put in place.

The lab scale microwave plasma cracking system was designed, assembled, tested and is shown in Figure 8. This system uses ethane as the hydrocarbon, and argon as the carrier gas. The flow rate for each gas is independently managed using a mass flow controller (both of which are controlled and recorded through LabView, a controls program. LabVIEW is also used to monitor and record inlet gas temperature, outlet gas temperature, pressure inside the system along with the microwave power and cooling water temperature. As a safety feature, an emergency stop button is located in the LabVIEW interface, which immediately shuts off the hydrocarbon gas flow and microwave energy. A Lexan safety shield is located in front of the hot zone of the quartz tube, which also incorporates microwave shielding.

Figure 7 Microwave surfaguide component of the microwave plasma system ordered from Gerling Applied Engineering

Figure 8 A) Digital image of the microwave plasma system built in Ceralink's lab. B) Close-up of the microwave

Ceralink rented a gas chromatograph (GC) for analysis of the hydrocarbon products during the laboratory testing phase of this project (Figure 9). The equipment was obtained from Edison Analytical Laboratories, run by Dr. James Carnahan, a retired Chemist from General Electric. Dr. Carnahan also served as a consultant and provided assistance in setting up and running the GC, along with the experimental analysis. The gas chromatograph (GC), model HP 5890A, was fitted with a thermal conductivity detector (TCD) and used argon as carrier gas. The GC was used for analysis of the hydrocarbon products during the laboratory testing and provided the composition of the cracked gas for the following components: H_2 , CH_4 , C_2H_2 , C_2H_4 and C_2H_6 . Any species heavier than ethane in the effluent would not be detected.

Initially, the GC was placed next to the microwave plasma system, and sampling was done directly from the exhaust line. However, it was observed that noise from the plasma column was interfering with the GC. The GC was moved to the other side of the lab in order to utilize a syringe method for gas sampling during the plasma runs. For the non-plasma experiments, the GC was relocated next to the microwave cracking system so that samples could again be taken directly from the exhaust line of the reactor tube and introduced into the GC through a gas sampling valve, minimizing contaminants. It was calibrated using a gas standard containing 10% hydrogen, 10% methane, 30% ethylene, and 50 % ethane.

Figure 9 A) Digital image of the gas chromatograph (GC) and sample analysis workstation. B) Close-up of the GC and sample analysis system.

Figure 10 A) Digital image of a plasma in Ceralink's lab scale system. B) Close-up of the microwave plasma in the reactor chamber.

Microwave Plasma Runs

Initial exploratory runs shown that a microwave plasma could be successfully generated in this system, as shown in Figure 10. Initial plasma experiments were performed, exploring the plasma behavior and color change with different ratios of ethane and argon. The microwave reactor at Ceralink was operated with three degrees of freedom: 1) flow rate of argon (via mass flow controller), 2) flow rate of ethane (via mass flow controller), 3) temperature (via electrical microwave input).

For the microwave plasma experimental results, the data in Figure 11 shows selected laboratory scale microwave plasma ethane cracking experiments where ethylene was produced. For each run, a microwave-plasma was ignited using an argon flow of 200 ml/min. Once the microwave plasma ran continuous for 30 seconds, ethane was introduced in six second pulses, at a flow rate of either 30 or 60 ml/min. The ethane was pulsed, as a steady flow of ethane extinguished the plasma. Samples were collected using a syringe as they exited the plasma reaction tube and analyzed using a gas chromatograph. Figure 12 shows data from the gas chromatograph analysis for three different run parameters. It is possible to compare the yield after cracking for each hydrocarbon and also look at the conversion and selectivity.

The conversion percentage is defined as the amount of ethane converted into product. The ethylene selectivity is defined as the amount of ethylene produced from the overall product. Higher ethylene selectivity is desired, as it means more efficient production. Figure 13A below shows the conversion of ethane to ethylene was higher at the higher ethane flow rate (60 ml/min) and *higher* microwave power

level (750 W). The total conversion of ethane to products (from left to right) was 96%, 99% and 15% conversion. The area in black is the unconverted ethane feed. Even though the conversion percentage was high for the first two, the selectivity to ethylene was lower as a large amount of hydrogen was produced. Figure 13B shows that the ethylene selectivity was better at 60 ml/min ethane flow and *lower* (200 W) microwave power. This is because ethylene was the main product, but unreacted ethane still remained. This data indicates that 1) a longer residence time may be required at the 200 W to react more of the ethane, or 2) a slightly higher microwave power may increase the product conversion, while maintaining high ethylene selectivity. The lower microwave power is preferable for scale-up, as the energy efficiency will be better with lower energy consumption.

One challenge was maintaining plasma with a continuous flow of ethane. A continuous flow of ethane is preferred for improving the experimental method of analyzing the reactants and further developing the process. A series of experiments were conducted to explore the lowest flow rate of ethane possible, to allow a continuous flow without extinguishing the plasma. It was found that the plasma was extinguished with a continuous flow of ethane even at extremely low flow rates, down to 3 ml/min. Part of the issue was that the ethane mass flow controller produced a large pulse of ethane upon first opening the valve, which may have caused the plasma to go out. Increasing the flow of argon up to 200 ml/min did not produce a stable plasma with 3 ml/min of ethane flow. Due to the fact that the ethane was pulsed and a steady state reaction was not maintained, it was difficult to determine the amount of actual ethane present in the system. The below figures are best estimates. It was also difficult to know what point in the reaction the samples for the GC were being taken.

Figure 11 Analysis of products from cracking ethane in the microwave plasma at different flow rates and microwave powers; 30 ml/min (red graph) at 750 W, 60 ml/min (blue graph) at 750 W and 60ml/min (green graph) at 200 W.

Figure 12 Amount of ethylene produced compared to all gaseous products for two different ethane flow rates and microwave power levels.

Figure 13. A) Ethane feed to product conversion after microwave plasma cracking. Note, the 30 ml/min at 750 W had the highest product conversion, however, most of the product was hydrogen instead of the desired ethylene product .B). Selectivity of all product gases after microwave plasma cracking. Note the 60 Selectivity of all product gases after microwave plasma cracking. Note the 60 ml/min at 200 W had the highest selectivity to ethylene.

Microwave Carbon Susceptor Runs

In this set of runs, an alternative system configuration was used. It was concluded that there was insufficient time in this program to studying the control of the plasma arc in order to maintain a steady state system. Similarly, experiments at ambient pressure resulted in residence times that were too long and the ethane over-cracked to form hydrogen and carbon. Therefore, the data presented below was performed under vacuum with microwave heat input into the reactor in the absence of a plasma arc. It is likely however, that a microwave reactor could be designed to operate at elevated pressures and using plasma arc if so desired.

For this second configuration, the initial experiment started with a fresh quartz tube (no carbon) and employed a microwave-generated plasma arc inside the reactor. It is important to note that for the conditions of the experiments, microwave exposure alone was not sufficient to crack the ethane feed. A microwave-generated plasma was induced in the reactor zone at the start-up of operation to light off the cracking reactions. After a thin layer of carbon formed on the surface of the quartz tube, the plasma was extinguished and continued microwave exposure was sufficient to continue the cracking reactions. It is theorized that the carbon layer is heated by the microwaves and this heat allowed the cracking reactions to proceed without the need to sustain a plasma phase in the reactor. The optical pyrometer indicated a temperature reading in excess of 700 °C within 5 seconds of applying the microwave power (200 W). The quartz tube was used as the reactor vessel, which is microwave transparent (little to no heating). Carbon, especially a thin carbon coating is known to be a good absorber of microwave energy. It has been reported previously that amorphous carbon has heated by microwave to >1250 °C in less than 1 minute[5].

These runs were conducted under vacuum. The absolute pressure at the reaction zone outlet was a function of the inlet flow rate and ranged from 15 – 55 Torr. When the flow rate was adjusted higher, there was a corresponding increase in the reactor pressure, as the vacuum pump was set at all times to operate at full vacuum. These two effects nearly cancel so that the residence times were similar for most of the runs.

The temperature profile of the gas was not known precisely. A contact thermocouple placed an inch below and an inch above the microwave hot zone indicated low temperatures (< 150 °C); meaning the process gas underwent a rapid heating across the microwave zone and subsequent cooling from heat dissipation. An optical pyrometer aimed at the heated section of the quartz tube indicated a single temperature in the microwave zone (> 700 °C). This temperature reading was used as a guide rather than an absolute temperature of the reaction zone. It is believed that the gas reached temperatures well above the pyrometer measurement, perhaps 1000 °C or higher for the instances of high conversion of ethane. Evidence for this was the occasional (and accidental) deformation and melting of the quartz tube during ethane cracking at pyrometer readings of only 850°C.

The gas chromatograph (GC) provided the composition of the cracked gas for the following components: H₂, CH₄, C₂H₂, C₂H₄ and C₂H₆. Any species heavier than ethane in the effluent were not detected. The atomic molar hydrogen/carbon ratio of the reactor effluent was in the range of 3.0 – 3.1 for ethane conversions below 50%. This is good confirmation that the analytical measurements of the effluent were accurate because the effluent H/C ratio was the same as the feed ethane. At higher conversions of ethane, the associated H/C ratio of the effluent increased to the range of 3.2 – 3.3 mole/mole. This indicates that components heavier than ethane were in the reactor effluent but not detected by the GC. For example, if benzene was formed at high conversions of ethane, then the quantity of H₂ in the effluent would increase while the carbon-containing benzene would not be detected; this would lead to an H/C ratio greater than 3.0 of the effluent mixture as measured by the GC.

The experimental results were compared to simulations performed with Technip's proprietary SPYRO[®] program, the industry standard for hydrocarbon pyrolysis modeling. SPYRO[®] is recognized for its ability to simulate industrial operations. The ISO version of SPYRO[®] was developed for the purposes of simulating laboratory conditions like those at Ceralink. The ISO version of SPYRO[®] uses its kinetic model to predict yields as a function of residence time, pressure and temperature only – the reactor dimensions are not required. The model is quite stable and predicts yields under conditions such as those above, namely: argon rather than dilution steam, vacuum pressure, and very high temperatures.

Since the actual time-temperature profile in the reactor was not known, an approximation of the residence time was taken to be 0.001 seconds. This is very short by industrial standards and is a result of the very

low absolute pressure in the reactor and very short reaction length (< 1 cm). Based on this residence time assumption, and the ratio of argon to ethane in the feed (1 mole/mole), SPYRO[®] was run at various temperatures to illustrate the relationship between temperature and ethane conversion, as illustrated in Figure 14. The “S” shape curve shows the increase in conversion as temperature increases and a gradual tailing off of conversion at temperatures in excess of 1100 °C.

The yields of the measured components, as a function of ethane conversion, are provided in Figures 15a and 15b. The yields are presented in terms of ethane conversion because the actual residence time and temperature were not known to a high degree of certainty. The yield of ethylene increases with increasing conversion and reaches a maximum of 64 wt% yield at 95% ethane conversion; thereafter the ethylene yield drops off. The yields of hydrogen, methane and acetylene show similar trends up to 95% at which point methane and acetylene yields increase significantly with the loss of ethylene yield.

It is important to note that the yields presented from SPYRO[®] simulations have been re-normalized to include only those components which were measured by the GC. For example, at 70% conversion of ethane, SPYRO[®] predicts about 94% yield of hydrogen (H_2) through ethane (C_2H_6), the balance being predominantly C_3H_6 along with other higher hydrocarbons which were not detected by the GC. So to be consistent with the lab data, the SPYRO[®] yields of H_2 through C_2H_6 presented here have been renormalized to 100 %.

The experimental data are presented in the following figures. The agreement between the lab and SPYRO[®] is very good for hydrogen (Figure 16) and acetylene Figure 17. SPYRO[®] under-predicts methane (Figure 18) and ethylene (Figure 19) to some degree, but the data follows the shape of the SPYRO[®] curves nicely. It is expected that more detailed GC analyses would result in an even closer match to SPYRO[®]. Considering the limited time available for the experimental program, the quality of the data seems to be quite high.

In summary, the experimental program established that microwave energy can be used to supply the endothermic heat required for the pyrolysis of hydrocarbons to olefins. The experimental results were in-line with simulations using the SPYRO[®] program suggesting that microwaves neither enhance nor inhibit the pyrolysis chemistry. Microwave generation requires electrical input which is inherently less efficient compared to energy generated from combustion of fuel gas as is currently employed in industry. However, conventional heat transfer necessitates many parallel reactor tubes because of limitations on heat flux because of the resistances to heat transfer and the temperature gradient from the hot combustion gas to the cooler process gas. There may be advantages of microwave heat transfer compared to conventional heat transfer which relax current constraints and thereby allow novel reactor designs that result in more efficient production of ethylene. Those design exercises were beyond the scope of this project. In addition to industrial reactor design, it would be very interesting if further experimental work could be performed at elevated pressures and with the use of dilution steam to aid the microwave heat transfer mechanism.

Figure 14. SPYRO[®] Predicted Ethane Conversion at 42 Torr and 0.001 Seconds Residence Time

Figure 15A. SPYRO[®] Predicted Yield of Ethylene at 42 Torr and 0.001 Seconds Residence Time

Figure 15B. SPYRO® Predicted Yields for Hydrogen, Methane and Acetylene at 42 Torr and 0.001 Seconds Residence Time

Figure 16. SPYRO® Predicted and Measured Yields Hydrogen (H₂)

Figure 17. SPYRO® Predicted and Measured Yields Acetylene (C₂H₂)

Figure 18. . SPYRO® Predicted and Measured Yields Methane (CH₄)

Figure 19. SPYRO® Predicted and Measured Yields Ethylene (C₂H₄)

Task 4. Modeling and Design of Microwave System

Modeling work began in December 2010. Over the next few months, our research team worked with Dr. Jeff Braunstein of Rensselaer Polytechnic Institute to conduct microwave modeling of the plasma process. One of our research team members, Inessa Baranova, created a 3-D base model in GID, Figure 20, which was then coded by Dr. Jeff Braunstein. This shows a simplified version of the laboratory scale microwave equipment from Figure 7.

Dr. Braunstein's model was based on some previous microwave modeling code, which was modified to simulate a plasma feed microwave system. Three significant changes/modifications to the microwave heating program were made to simulate this new system and to make the program more user friendly. The user interface (UI) was modified to improve interaction with the program. A first order estimate of mass transport was implemented. A radiation condition is being implemented, representing the finite simulation domain of an infinite space. The changes to the UI were implemented to facilitate the entry of material properties and flags. A new program was also developed, replacing the need to edit text files. The material database program is now customizable, allowing new materials and new material properties to be entered as necessary. The input screen can be selectively configured for different models, as the user sees

fit. Flags regarding material domain properties are available and can also be added as new physical models are considered. This aspect will result in more 'plug and play' algorithm development where new code subroutines can be added with minimal revision to existing code.

Figure 20. Computer drawing of the 3-D model made using GID for the microwave model development plasma reactor chamber.

I. Model Results (see appendix A for a description of model theory)

Images of the field distribution inside the waveguide resonator are included. The images are cross-sections along the axis of the waveguide. Temperature profiles in the region of the plasma formation are shown, again cross-sections in the x-y, and y-z plane.

a. Initial Model

The initial design investigation treated the problem as a standard heat absorption study with a lossy dielectric. While this investigation was not consistent with the experimental implementation, it was useful for testing some of the numerical concepts. The study involved microwave power absorbed by gas flow in a cylindrical tube. In order to observe a significant temperature rise, it was assumed the gas was flowing very slowly and that ionization occurred when sufficient energy had been absorbed. In this initial study, the slow moving assumption was necessary since the loss component of the gas is small enough that using a dielectric model results in a slow temperature rise. This study was intended to test some of the model characteristics. A model more consistent with the experiment will be discussed next.

On the following Figures (Figure 21, Figure 22, & Figure23), the magnitude of the electric field and the temperature is shown for different time stages under the assumption that the dielectric properties of the gas are changing with time as the temperature of the region increases. The images are cross-sections where the quartz tube intersects the applicator. In each set of figures, the three images are described as follows:

- a) Magnitude of the electric field in an xy -plane (horizontal) slice through the center of the narrow section of the waveguide applicator
- b) Temperature in an xy -plane (horizontal) slice through the center of the narrow section of the waveguide applicator
- c) Temperature in an yz -plane (vertical) slice through the center of the narrow section of the waveguide applicator

*It is assumed that power is only absorbed in the gaseous region. Therefore, initial temperature growth only occurs in this region. Heat diffusion results in temperature grown in the surrounding medium, including into the air region of the waveguide. For these simulations, the quartz tube was not part of the simulation.

Figure 21. Electric Field and Temperature profiles

Figure 22. Electric Field and Temperature profiles

Figure23. Electric Field and Temperature profiles

b. Induced Plasma Model

The model was refined to accommodate the experimental technique of plasma excitation. In the experiment, initial ionization was achieved using a Tesla coil. This technique was used to produce an ionization arc. Rather than implementing a numerical model of the arc, an ionization region is introduced in the region where the quartz passes through the waveguide applicator. The dielectric properties in this region are assigned using the complex permittivity and complex conductivity discussed previously. An estimated electric field strength is used as threshold value necessary for maintaining the plasma. If the field strength is too low, it is assumed the region cannot maintain ionization and the dielectric properties of Argon gas are applied. Based on these approximations, the finite element method is applied to the geometry. The resulting field calculations are re-applied to determine regions where ionization occurs. The dielectric properties are re-assigned to the elements based on the new calculation and the field is determined again. This process is repeated iteratively until the plasma region has been defined with no new elements being calculated in the ionization region.

The following Figure 24 indicates the ‘length’ of the plasma region, defined as the approximate distance in the quartz tube that the plasma has been excited. The variable factors are the applied power and the plasma frequency. As indicated previously, for the source frequency of 2.4 GHz, if the plasma frequency is reduced the conductivity term is reduced and the dielectric properties approach those of air. The source power affects the magnitude of the field in the waveguide, which will in turn affect the magnitude of the field that propagates into the plasma column, increasing the size of the plasma.

Figure 24 ‘Length’ of the plasma column as a function source power and plasma frequency

On the following page, the electric field in a yz-plane centerline (vertical) slice is shown. Figure 25a represents the zero plasma state, with the dielectric constant in the gas slightly above air. Figure 25b and c are plots for a plasma frequency of 0.8 GHz with ionization thresholds at 200 V/m and 400 V/m respectively.

Figure 25. : Electric field magnitude for various plasma frequencies.

Tasks 5 and 6, see Benefits Assessment

Benefits Assessment

The chemical industry consumes 6.5 quadrillion BTU's of energy each year. This constitutes roughly 20% of all industrial processes within the US. This substantial energy consumption makes the chemical industry a prime target for new and innovative technologies that will drastically reduce energy consumption. Within the chemical industry one process stands out as a substantial energy consumer. The production of ethylene, propylene and its constituents for use in plastics and resin manufacturing demands 1.3 Quadrillion BTU's annually, which is equivalent to approximately 20% of the energy used by the chemical industry. Production of ethylene, propylene and its constituents required a complex manufacturing facility involving several stages of heating, cooling, and separating. Upon close inspection of the production facility it is observed that nearly half of the energy used is dedicated to heating the hydrocarbon feedstock. This indicates 750 Trillion BTU's annually goes into heating hydrocarbon feedstock for the cracking process. Industry estimates that the hot section of a cracking facility is typically 45% efficient. As a result, only 1 BTU of energy is transferred and used in the reaction process for every 2.2BTU's of heat input. This results in nearly 420 Trillion BTU's of waste heat annually from this process alone.

Direct microwave heating technology is expected to reduce the energy required for cracking by 50-75% and save 10-15% of the total energy used in the chemical processing industry. This savings is equivalent to nearly 195 Trillion BTU's 2020, by capturing 10% of the ethylene production market (28.3 MM tons/yr), see Table 1. This reduction in energy consumption will bring the energy demand for the production of ethylene down from 64 million BTU's per Metric Ton to less than 30 million BTU's per Metric Ton. A 10% market conversion is roughly equivalent to 16 microwave based ethylene crackers with an average output of 150,000 tonnes/year.

Reduction in Green House Gas Emissions

This new method of direct microwave heating will also significantly reduce greenhouse gas emissions, especially emission of CO₂. A large portion of the CO₂ emission savings will be derived from the energy savings stated above. Based on Table 1 below it is projected that CO₂ emissions will be reduced by 35 million Metric Tons annually. Also contributing to this reduction in emissions is the reduction of coke formation (as CO₂ is a major bi-product of the decoking process). As with the energy savings, this reduction in emissions would be felt upon installation of the final technology and would continue to be realized as the technology continues to save energy and emissions each successive year. Furthermore the transition to direct microwave heating would be a transition to electrical power sources rather than on site combustion fuel sources. With regulations already in place in the power generation industry, and the efforts that industry has already put into place to minimize CO₂ emissions, there would be even further reduction in emissions over the currently used conventional heating methods. Essentially, there would be no local emissions, allowing for better control and easier emissions regulations.

Potential Economic Benefit and Market Impact

The sky rocketing prices of standard energy fuels has led to large increases in costs of production within all manufacturing industries, especially for highly energy intensive processes. In a similar fashion, a technology that offers drastic energy savings would reduce costs to manufacturing tremendously. The above stated energy savings of 50-75% within the cracking portion of an ethylene and propylene production facility would be directly linked to cost savings at the same level. The market benefit to the US economy can be estimated based on the reduced fuel requirement. The current price of natural gas (primarily used to heat the metal tubes) is \$4.48/MMBTU[6]. Multiplying the cost of fuel by the amount

of projected energy savings (195 Tril BTU) is equal to \$874 million dollars per year. This number represents fuel savings alone. Ceralink anticipates this number to increase as the value of other benefits, such as increased product yield and decreased coking are quantified and added in.

Table 1 Projected Annual Energy and CO₂ Savings for Implementation of a Microwave Hydrocarbon Cracking Process for Ethylene Production in the year 2020.

Year	Energy (TBTU/yr)	Environmental Benefit CO ₂ (Mlb)	Economic Benefit (\$/yr)
2020	195	22,815	874 MM

Validity of Assumptions and Estimates

The energy assumptions used in this proposal are based on a wide array of studies involving microwave enhanced chemical processing and the energy savings observed. A conservative estimate of 50% energy savings was used for calculation purposes.

Typically microwave enhanced chemistry has even greater energy savings on the order of 75% and up to 90% [16, 17]. The energy intensity numbers for ethylene production and its various steps were taken directly from a Department of Energy study [1]. The 50% energy savings was applied only to the energy used in the heating of the feedstock even though other parts of the process will also be improved with this technology. The reduction in cooling requirements due to the reduction in tube temperature will reduce energy demands. The reduction in coke formation will keep reactors at peak efficiency and keep them on line for longer stretches of time. All of these factors contributing to the reduction of energy make the targeted goal well within the expected capabilities of this proposed technology.

Carbon dioxide emissions were primarily based on savings to fuel consumption. It was assumed, based on Table I. that the average fuel consumed emits 150lbs of CO₂ per 1 million BTU's of fuel burned. This number was used to convert the energy savings to CO₂ savings. As stated above there are also other factors contributing to emissions reductions which makes the assumptions easily attainable with the proposed technology.

Commercialization

Market Analysis

US demand value of ethylene increased from 16,634.4 MMTPA in 2000 to 18,437.3 MMTPA in 2010 at a CAGR of 1.03%. According to GlobalData forecasts, the demand for ethylene is expected to grow from 18,437.3 MMTPA in 2010 to 34,558.3 MMTPA in 2015 at a CAGR of 11.04% for the period, as shown in Figure 26[7].

The major ethylene producers are Chevron Phillips Chemical Company LLC, LyondellBasell Industries AF S.C.A., Exxon Mobil Corporation, The Dow Chemical Company, and Royal Dutch Shell plc. Together these companies accounted for 73% of the ethylene capacity in US in 2010[7]. The plant capacity of the company is calculated on the basis of its equity stake in the plant. Other companies that are active in the US are INEOS Group Ltd, Westlake Chemical Corporation, Formosa Plastics Group and Eastman Chemical Group etc.

In the US, Thermal Cracking is the dominant process used for ethylene production. In 2010, it accounted for 95% of the installed ethylene capacity of 27.35 MMTPA in the region. The next dominant process in the region was Catalytic Pyrolysis. It accounted for 5% of the installed ethylene capacity in the region.

Our industrial partner, Technip was responsible for 11% of the total installed capacity of 27.35 MMTPA in 2010. In the US, Dow Chemical Company's ethylene plants in Freeport and Plaquemine use Technip Ethylene technology [7]. Technip is an important US and world wide designer of ethylene plants.

Table 2. US, Ethylene Industry, Installed Plant Capacity by Technip Ethylene Technology, 2010[7]

Plant Name	State/Province	Plant Start YYYY	Annual Capacity (MMTPA)
The Dow Chemical Company Freeport Ethylene Plant 1	Texas	1982	0.630
The Dow Chemical Company Freeport Ethylene Plant 2	Texas	1982	1.010
The Dow Chemical Company Plaquemine Ethylene Plant 1	Louisiana		0.520
The Dow Chemical Company Plaquemine Ethylene Plant 2	Louisiana		0.740

The main Commodities that consume ethylene in the US are Polyethylene, Ethylene Dichloride (EDC), Ethylene Oxide (EO), Vinyl Acetate Monomer (VAM), Styrene Monomer and Alpha Olefins. In 2010, these Commodities together accounted for 94% of the ethylene demand in the region. The ethylene market in the US is dominated by the Polyethylene. In 2010, this market accounted for a share of 50%. It was then followed by other commodities such as Ethylene Dichloride (EDC), Ethylene Oxide (EO) with share of 15% and 13% respectively. The other remaining markets accounted for 22% of the share in 2010.

The critical need that the microwave technology offers is that of producing significant energy savings in the form of reduced natural gas consumption and the potential for higher throughput using existing infrastructure. The value proposition being offered by the technology is that end-users can reduce their energy consumption due to kiln operations by up to 50% and potentially increase their product selectivity.

Figure 26. US Ethylene Industry Market Size 2000-2015

Market Barriers

Microwave technology has some market barriers to entry that will continue to be minimized through continued research, pilot, and demonstration-scale technology investments being pursued over the next several years. Within the olefin producing industries, significant capital infrastructure is in place and resistance to completely scrap the current furnace box technology. Ceralink has structured its research, development, and deployment plan to focus on rather low impact retrofits to the heating zone of the process that still result in impressive potential energy savings.

Competition

The petrochemical industry has long been recognized a dominate consumer of thermal and electrical energy in the United States. Specifically, petroleum refineries consumed 6,692 trillion BTUs and 37.155 TWh in 2006 [8]. Ren et al[9] had declared the pyrolysis section alone to be the most energy intensive, accounting for 65% of the total energy used and 75% of the total energy lost throughout the cracking process. Seeking to reduce the industry's consumption, improvements upon traditional technologies have historically provided marginal benefits in energy consumption and efficiency, however significant improvements cannot be made without a novel new approach of supplying energy to hydrocarbon streams. The major competition arises from the industry standards, and industry reluctance to be the first to incorporate a new technology and move away from fire boxes used in thermal steam cracking and catalytic cracking.

Marketing and Commercialization Approach

The approach for commercialization of this technology will require continued research and development to prove out the merits of the process and refine the benefit projections. From this initial phase of project work, Ceralink and Technip have a joint development agreement in place. Ceralink will seek funding to continue this work from several sources, including Technip, Department of Energy and the New York State Energy Research Development Authority (NYSERDA), see Table 3. Ceralink would like to transition the technology lead to Technip, who is well positioned to incorporate the developed microwave technology into their current ethylene crackers and introduce the technology to industry customers. Ceralink would continue the research effort on the laboratory scale, with a transition to a pilot scale. Eventually, the finalized technology would be completely transferred to Technip and Ceralink would receive a royalty for each ethylene cracker the microwave technology is incorporated into.

The proposed technology would be first designed as a retrofit technology, which would keep initial startup costs to a minimum allowing nearly all current manufacturing facilities to convert their plants with little investment risk. Upon implementing the retrofit technology, a manufacturing site would see immediate cost cuts in energy consumption that are directly related to cost cuts in the entire manufacturing process. Further developments to the technology would involve new facility designs that would be more economical with the reduction in footprint, refractory materials and emission controls.

Table 3. Projected investment plan for microwave cracking technology

Funding Profile				
	FY11	FY12	FY13	FY14
DOE Office Investment	220,000			
Industry partner	40,000	\$200,000	\$800,000	\$1 M
Microwave/RF Co.		\$ 50,000	\$200,000	\$200,000
Project Total	260,000	\$250,000	\$1 M	\$1.2 M

Market Impact

The chemical industry consumes 6.5 Quadrillion BTU's of energy each year. This constitutes roughly 20% of all industrial processes within the US. This substantial energy consumption makes the chemical industry a prime target for new and innovative technologies that will drastically reduce energy consumption. Within the chemical industry one process stands out as a substantial energy consumer. The production of ethylene, propylene and its constituents for use in plastics and resin manufacturing demands 1.3 Quadrillion BTU's annually, which is equivalent to approximately 20% of the energy used by the chemical industry. Production of ethylene, propylene and its constituents required a complex manufacturing facility involving several stages of heating, cooling, and separating.

Technip, the commercial partner on this project, was extremely excited about the results from this quarter. Ceralink and Technip have entered discussions on a follow-on project. Once an agreement has been reached, Technip will provide research funding for continuation of work on the microwave plasma laboratory system modification for continuous flow ethane, data acquisition, and analysis. The follow-on project will likely include the design of a next scale prototype.

Ceralink is actively developing technologies to address materials needs in the market, and teaming with appropriate equipment manufacturers to make technologies available to industry. For example, Ceralink assisted BASF (formerly Engelhard) is procuring a \$5 million grant from the Department of Energy for reclamation of precious metals from used fuel cell membranes. Ceralink was a subcontractor on the project, and responsible for developing the microwave digestion method for 99% precious metal recovery. Ceralink successfully achieve this goal, in addition to developing a novel method for separation of MEA membrane layers. A patent on the separation method is pending. BASF has set up a pilot scale facility at their Iselin, NJ research center, based on the work performed with Ceralink.

It is projected that the first industrial pilot system could be implemented by 2016. The time required to see the energy reducing effects to take place is only limited by the time it takes to develop the technology and implement it into current manufacturing facilities. It is expected that the technology will be developed to an industrial scale retrofit marketable component in the next 5-7 years. Installation in a manufacturing facility will produce immediate results within that facility. After the first industrial demonstration, uptake into industry is expected to follow exponential growth over the next 7-10 years as this technology becomes the new industry standard.

Accomplishments

Accomplishments by quarter:

In the first quarter, the primary accomplishments included putting the contract between Ceralink and DOE in place and finalizing the Statement of Project Objectives. The process of creating subcontracts/work plans with the project partners were also initiated.

The primary accomplishments in the second quarter:

- Completed Kick-off call with DOE
- Visited Technip for in-depth discussion with their scientists
- Expanded research in cracking system designs and research into dehydrogenation
- Planned for lab-scale testing and ordered equipment
- Conducted initial energy assessment

The primary accomplishments in the third quarter were:

- Attended 23rd annual Ethylene Producers Conference
- Met with Industrial partner

- Received and set up lab-scale equipment
- Met with University partner to discuss modeling progress
- Developed design for a scale up microwave plasma array

The primary accomplishments in the fourth quarter:

- Completed assembly of the Microwave Hydrocarbon Cracking System
- Outlined a designed experiment
- Moved all experimentation processes in-house
- Ran baseline and gas standard experiments for familiarization
- Developed additional designs for a scale up microwave plasma application

The primary accomplishments in the fifth quarter, we:

- Conducted laboratory scale ethane cracking experiments
- Produced ethylene from the microwave plasma system
- Manipulated variables to explore product output
- Developed and refined conceptual scale-up equipment designs
- Met with DOE project managers at Ceralink
- Submitted a paper for the 24th annual Ethylene Producers Conference

Conclusions

This project demonstrated microwave cracking of ethane with good product conversion and ethylene selectivity, with a short residence time (~0.001 sec). The laboratory scale equipment was designed and built, along with concept designs for larger scale implementation. The system was operated below atmospheric pressures, in the range of 15 – 55 torr, with argon as a carrier gas. The measured products included hydrogen, methane, acetylene, and ethylene. The results followed similar trends to those predicted by the modeling software SPYRO[®], with the exception that the microwave appeared to produce slightly lower amounts of ethylene and methane, although enhanced analytical analysis should reduce the difference. Continued testing will be required to verify these results and quantify the energy consumption of microwave vs. conventional. The microwave cracking process is an attractive option due to the possibility of selectively heating the reaction volume rather than the reactor walls, which may allow novel reactor designs that result in more efficient production of ethylene. Supplemental studies are needed to continue the laboratory testing and refine processing parameters.

Recommendations

It is recommended that this work be continued in order to further explore the microwave processing conditions with respect to flow rate, pressure, and microwave power. Considering scale-up, it would be advantageous to find operating conditions closer to ambient pressure, where good product conversion could still be maintained. It would also be beneficial to decrease or omit the argon carrier gas. Steam could be explored as a dilution medium, which is in line with current industry practice. A longer column for the gas chromatograph could be obtained to identify species heavier than ethane, for a more complete picture of the reaction kinetics, and a better comparison to the SPYRO[®] model.

Follow on work should also focus on refining a pilot scale microwave cracking system design, which would be based on the results of the continued laboratory scale testing. Additional input from Technip would be required to explore retrofitting of certain types and size conventional ethylene crackers. Technip would be involved in the pilot scale microwave cracker design, as well as identification and quantification of the benefits for using microwave cracking.

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Appendix

Appendix A: Description of the microwave model

II. Physical Model

A brief discussion of the electromagnetic characteristics follows. Initially, a derivation of the wave equation is provided and the dependency on material properties is discussed. The properties of a wave guide resonator are presented with comments on the shallow/wide waveguides. The heat diffusion equation is presented along with its application in the resonator system. The dielectric characteristics of the plasma are discussed.

a. Wave equation

Electromagnetic propagation is characterized by solutions to Maxwell's equations. In a source free region, the vector form of the time dependent equations are written as

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad \text{and} \quad \nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t}$$

where B is the magnetic flux, E is the electric field, D is displacement field and H is the magnetic field intensity. Since

the source in this investigation can be considered AC steady state, $\propto I_{source} e^{(j\omega t)}$ resulting in the derivative

operations having the equivalent form $\frac{\partial}{\partial t} \rightarrow j\omega$. Maxwell's equations can then be rewritten

$$\nabla \times \vec{E} = -j\omega \vec{B} \quad \text{and} \quad \nabla \times \vec{H} = j\omega \vec{D}$$

Since the material is assumed to be non-magnetic, the magnetic flux is linearly related to the magnetic field intensity, $B = \mu_0 H$. In the air region, the electric field and displacement field have a similar relationship, $D = \epsilon_0 E$. In the plasma region, the relationship is more complex and a dielectric properties are a tensor, in which the relationship between the field components depends on the excitation direction of the plasma and orientation of the field. A first order approach is to consider the plasma excitation in a single direction, oriented along the axis of the tube. Taking the curl of both sides, Maxwell's equations can be combined

$$\nabla \times \nabla \times \vec{E} = -j\omega \nabla \times \vec{B} = -j\omega \mu \nabla \times \vec{H} = \omega^2 \mu (\vec{\epsilon} \vec{D})$$

In this equation, the permittivity is shown as a tensor. However, an isotropic approximation will be used, a discussion of which is provided in the section on numerical applications.

b. Heat Diffusion

Determination of heat diffusion is determined by the scalar partial differential equation.

$$q = c\rho \frac{\partial T}{\partial t} = k\nabla^2 T + f(t)$$

where, q is heat flow, c is the specific heat, ρ is the density and k is the thermal diffusion constant.

This equation does not include heat migration due to the flow of the gaseous plasma. In the region of gas flow, the diffusion equation effects are considered nominal. Instead, temperature is determined by the energy absorbed from electromagnetic field. Heat exchange is present at the quartz interface, determined by the flow rate and temperature difference.

Boundary conditions are a significant part of the model, where both convection and radiation losses can be significant. Convection losses are especially relevant at gas-solid interfaces. The convection boundary condition is defined by the differential equation

$$q = h_r (T_1 - T_2)$$

where h_r is the heat transfer coefficient, T_1 and T_2 are the temperatures on either side of the boundary. The heat transfer coefficient is typically difficult to determine analytically and estimated values are often applied.

The radiation boundary condition is defined as

$$q = \varepsilon \sigma (T_1^4 - T_2^4)$$

where ε is the emissivity, σ is the Stefan-Boltzmann constant, T_1 and T_2 are the temperatures on either side of the boundary.

Radiant heat can be a significant aspect in plasmas, where plasma temperatures can be quite large. Due to the complexity of determining the plasma temperature, the current numerical model neglects radiation losses. Determination of this term is planned as a future revision.

c. Waveguide Characteristics

The resonating waveguide is designed to propagate a TE01 mode, the lowest frequency mode that can propagate without attenuation in a rectangular waveguide. Geometric discontinuities will result in the local excitation of other modes, perturbing the field in that region. These excited modes will attenuate in the region away from the discontinuity, where the guide is smooth and rectangular, but can have a physical impact local to the discontinuity. The resonator geometry in this project includes a gas/plasma filled tube in a region where the height of the waveguide is reduced significantly (include or reference figure). This geometry produces a region where the E_x and E_y field components are attenuated very rapidly. In this region, the strong E_z component is parallel to the axis of the plasma tube. This geometry allows some simplifications when considering the dielectric tensor in the wave equation. Further discussion follows in the section on dielectric properties.

d. Dielectric Properties of Plasmas

At low pressure, argon gas has dielectric property near those of air with a slightly larger loss term. As mentioned above, in a simple heating model power absorption would be quite slow. However, once the gas is ionized, the dielectric properties become more complicating. Considering a complex permittivity

$$\varepsilon = \varepsilon_o \left(1 - j \frac{\sigma}{\omega \varepsilon_o} \right)$$

where ε_o is the permittivity of free space, ω is the radial frequency of the source and σ is the conductivity of the material.

A first order approximation can be used, where the dielectric depends on the plasma frequency such that

A more sophisticated approach considers a complex conductivity

$$\sigma = \frac{e^2 n_e}{m_e} \frac{1}{\nu_{eff} + j\omega}$$

where ν_{eff} is the collision frequency of the electrons.

e. Power Absorption

When considering lossy dielectrics, the power absorbed is proportional to the imaginary term of the dielectric and the electric field magnitude squared. The forcing term in the heat equation can then be approximated as

$$f(t) = \frac{1}{2} \varepsilon_o \varepsilon_{imag} |E|^2$$

The above equation is applicable for dielectric losses in a bulk material. Ohmic losses due to current excitations can be present. In solid low-loss dielectrics, ohmic losses are typically negligible relative to the dielectric losses due to polarization. In plasmas, current flow due to magneto-hydrodynamic effects is present and contributes a to the loss term. This approximation was used as an initial approximation when treating the problem as a classic dielectric heating problem.

When considering power absorbed by the plasma, the conductivity term in the preceding section provides an appropriate expression

$$P = \frac{1}{2} \text{Re} \left(\frac{e^2 n_e}{m_e} \frac{1}{\nu_{eff} + j\omega} \right) |E|^2$$

In the simulations, the power absorbed must be sufficient to maintain the plasma. In the plasma, power is lost via collisions, diffusion and radiation. One way to view this relationship is that a threshold electric field is required to maintain the plasma. This approach was used in the simulations.

III. Numerical Model

The numerical approximations are presented in the following section. The finite element equation is applied to the electromagnetic wave equation. The heat equation is implemented on a finite difference grid. Gas flow is implemented on the same finite difference grid. A discussion of the application and limitation of piecewise constant interpolation of the material properties is included.

a. Finite Element Application of the Wave Equation

Application of vector identities to the wave equation results in the a reformulation given as

$$\int_{vol} (\nabla \times \vec{E}) \cdot (\nabla \times \vec{E}) dV - \omega^2 \mu \epsilon \int_{vol} \vec{E} \cdot \vec{E} dV + \int_{surf} \vec{E} \cdot (\hat{n} \times \nabla \times \vec{E}) dS = 0$$

This expression is applied to the discretized finite element mesh, with the integration over each element. Tetrahedral volume elements and triangular surface elements are used in the meshing algorithm. The electric field in each element is approximated with polynomial interpolation using edge elements. This type of element has the advantage of naturally enforced boundary condition for the electric field, such that E_{tan} continuity is maintained across region boundaries. Additionally, edge elements generally have greater stability in solution convergence as opposed to nodal elements and the associated necessary penalty function. The first two terms are applied in

b. Plasma Formation

An iterative process was applied to determine the plasma region. An initial estimate of the ionized region was assumed to be constrained to the quartz region. Based on this assumption, the dielectric properties of the plasma were established and the electric field was calculated as discussed above. Based on the estimate of the ionization field requirements, an approximate region of plasma formulation is determined. The dielectric properties are then recalculated and the electric field is recalculated. This process is repeated until the estimated plasma region is stable in the iterative process. The stability requirement is that no new elements are added to the plasma region. This requirement overcomes issues when convergence is 'close' and elements may toggle in and out of the plasma region.

c. Finite Difference Application of the Heat Equation

A standard finite difference method is applied to the heat diffusion equation. A first order forward method is used for the time derivative and a second order center method is applied to the second order space derivatives.

$$T_{i,j,k}^n = T_{i,j,k}^{n-1} + \frac{\Delta t}{(\Delta x)^2, (\Delta y)^2, (\Delta z)^2} \frac{k}{c\rho} \sum (T_{i+1,j+1,k+1}^{n-1} + 2T_{i,j,k}^{n-1} + T_{i-1,j-1,k-1}^{n-1}) + \frac{\Delta t}{c\rho} f^{n-1}(t)$$

where i, j and k are the cell indices

In this formulation, the forcing term is due to the absorbed power from the microwave energy. The power absorbed is described below. The finite difference grid volume defines the region over which the power is absorbed due to an external source, in this case the microwave power. In the above calculation, the time step must be sufficiently small such that the

d. Boundary Conditions

(boundary condition for both the electromagnetic system and diffusion equation,

e. Power Absorbed

The power absorbed defined in the above expression is defined on the finite difference grid. In each cell, the total power is defined as

$$P_{cell} = P_{i,j,k} \Delta x_i \Delta y_j \Delta z_k$$

where i, j and k are the cell indices. The approximate power is then the size of the cell multiplied by the power at the node. The power is calculated using the formula given previously. In the case of bulk dielectrics, the loss depends on the polarization terms. In the case of the plasma, the loss depends on the estimated conductivity.

f. Inhomogeneous Materials Distributions

Inhomogeneous materials have non-uniform material properties. In numerical methods, similar to the polynomial approximation of electric field, a polynomial fit must be applied to the material properties over each element. In this analysis, a piecewise constant fit was applied to each element indicating that permittivity and permeability are considered constant in the finite element equation. Jump discontinuities will exist across elements. The numerical method is viable, however, since the edge element application automatically enforces continuity of the electric field

vector between elements. A piecewise constant method then becomes equivalent to enforcing the tangential electric field boundary conditions at material interfaces. Piecewise constant approximations result in a reduced accuracy of the field calculation, though this effect can be offset by h-refinement of the tetrahedral mesh.

g. Gas Flow

Gas flow represents moving particles inside the geometric domain. The numerical equivalent representing gas flow involves a shift in the nodal temperatures of the finite difference mesh. The time scale of gas flow and heat diffusion were scaled together such that particles were shifted after the time step associated with heat diffusion was completed (figure below). This method allowed finite difference calculations without using a staggered or offset mesh. Additionally, by using discrete steps that are the same as the grid spacing, numerical inaccuracies associated with peak smoothing were avoided. The magnitude of the shift in the particles is dependent on the rate of gas flow. In the Figure, the (change in position) = (flow rate)(time step)

The code involved in this project was initially developed in 2007. The code considered a fairly simple domain of a nearly cubic metal enclosure. The microwave power was introduced via a rectangular aperture in the domain wall. This initial code was designed to study a fairly simple geometry and applied a number of simplifying assumption. Since that time, revisions have been steadily applied, some of which were intended to improve efficiency in algorithm performance, some to accommodate more complicated geometries and some to improve accuracy. During this project, software changes focused on improving the preprocessing algorithms and user interface.

a. Preprocessor revisions

Currently, the solid geometry is implemented and meshed using the GID software application. The software is used to generate triangular surface meshes and tetrahedral volume meshes. The region information is also indicated using GID. After generating the geometry data, numerical calculations are performed using developed Fortran applications running in a UNIX shell. The Fortran software inputs the GID geometry files and extracts the geometry data needed for finite element applications. Additionally, the finite difference mesh is generated during this stage. The initial implementation of the finite difference grid generation was fairly 'brute force' and inefficient when mapping the relationship between the finite difference grid and the finite element mesh. While the program can run in the background while doing other work, this algorithm was quite slow. A substantial speedup was obtained by taking advantage of the mesh connectivity in the search algorithms. The algorithm now requires approximately 10-20% of the computational time, which was very significant in dense meshes where the mapping could take hours.

b. Materials Database

In the current version of the software, a significant part of the problem definition is done via text files. This method is viable, but certainly is dated and not particularly user friendly in a modern computing environment. Introduction of a graphical user interface is intended and a first step in that process was the implementation of a materials database. The database is designed to develop a set of material ids and characteristics that only need to be defined once.