MICROPLASMA BALL REACTOR FOR LIQUID HYDROCARBON CONVERSION

A Thesis

by

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ABSTRACT

As the world's light oil reserves diminish, the use of alternative fuels is becoming more of a necessity. In order to make use of alternative fuels, alternative processes must be developed. The goal of this research is to convert long, complex chain liquid hydrocarbons into shorter, simpler chains. This is a method for converting heavy oils into lighter oils. The method used for this non-conventional processing uses a microplasma in order to initiate a cracking reaction and break up hydrocarbon chains.

A novel reactor was designed and tested with this application in mind. A high voltage power supply was hooked up to two parallel electrodes with a small metal ball trapped between them. Because the metal ball is a charged particle, the high electric field generated by the electrodes accelerates the ball toward the electrode of opposite charge. Right before contact between the ball and electrode happens; a small plasma discharge is created as the charge transfers between the ball and electrode. The ball, now of the opposite charge, is accelerated back to the original electrode. This process repeats to create a bouncing ball that produces rapid microplasma discharges which are used as input energy for the hydrocarbon cracking process.

This process was used to create a reactor with many balls bouncing in parallel for two separate applications. This reactor was first used to process JP-8, military jet fuel, and convert it to a propane rich mixture. The processing of JP-8 was able to produce a gaseous product that is up to 13% C_3 hydrocarbons by mass. Second, the reactor was adapted in order to process very heavy crude oils. These oils are very viscous and electrically conductive making them difficult to work with. By plasma processing at elevated temperature during treatment, permanent viscosity reduction by up to 40% was demonstrated by shortening the average hydrocarbon chain length. In order to increase the effectiveness of the processing a pressure vessel was used in order to keep lighter hydrocarbons in liquid phase. The producing of C_3 hydrocarbons from JP-8 and the lowering of the viscosity of heavy oil is evidence of reduction in hydrocarbon chain length.

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NOMENCLATURE

AC	Alternating Current
C	Celsius
C/H	Carbon to Hydrogen ratio
CNC	Computer Numeric Control
DARPA	Defense Advanced Research Projects Agency
DC	Direct Current
F	Fahrenheit
GC	Gas Chromatograph
HID	Helium Ionization Detector
JP-8	Jet Propellant 8
K	Kelvin
kg	kilograms
kJ	kilojoules
kV	kilovolts
L/D	Length to Diameter ratio
LPG	Liquefied Petroleum Gas
m	meters
mA	milliamps
MS	Mass Spectrometer
NATO	North Atlantic Treaty Organization

PID	Proportional Integral Derivative Controller
psig	pounds per square inch (gauge pressure)
PVC	Polyvinyl Chloride
UAV	Unmanned Arial Vehicle
VOC	Volatile Organic Compound
VR	Vacuum Residual

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1. INTRODUCTION

1.1 Background and Motivation

As the conventional crude oil reserves of the world get used up, efforts are being made to expand to using more energy sources. While the amount of light crude oil that is easily accessible is rapidly diminishing, companies are looking for new ways to extract, and process oil more efficiently. This has opened up the world to non-conventional oils. These heavy oils are more difficult to extract energy from than lighter crude oils are, but there are many more non-conventional oil reserves. These abundant non-conventional oil reserves require non-conventional processing so that the energy can be extracted in a useful form. Non-conventional oils are heavy and viscous making them difficult to refine and transport. Plasma technology has the potential to offer oil chemistry applications for non-conventional oil processing.

Because of the promising future of plasma chemistry in the oil industry, the work done in the thesis is funded by Chevron making much of the technology and processes used proprietary. In order to publish some of the technology developed and to initially study the microplasma ball reactor, an application to JP-8 was used. JP-8 is the only fuel that the military is allowed to transport because of its high flash point. There is a desire for the military to use propane fuel for cooking stoves or UAVs, and it would be useful if JP-8 could be converted on location into propane. In the case of both heavy crude oil and JP-8 a desired outcome is to reduce the average length of hydrocarbon chains in the fuel.

1.2 Thesis Statement

The goal of this research is to use plasma technology to reform liquid hydrocarbons. The objectives of this thesis are to discover how efficiently a microplasma ball reactor can convert JP-8 into a propane based mixture, and create a reactor that can reform heavy and viscous oils by reducing the average hydrocarbon chain length and decreasing the C/H ratio.

1.3 Thesis Overview

In section 2 background information on plasma will be discussed. The science of plasma chemistry and its applications will be explored. Previous research done using plasma chemistry to reform hydrocarbons, and its differences from this thesis will be highlighted. Lastly, the basics of the microplasma ball reactor will be described along with different advantages and challenges in developing this technology.

In section 3 the experimental setups used for the various experiments will be described and illustrated for both the JP-8 and heavy oils. The different diagnostic techniques will also be discussed in this section. In section 4, the results of each experiment will be discussed in detail along with their possible implications. In section 5, the findings and conclusions will be summarized and briefly explained along with ideas for future work.

2. DETAILED BACKGROUND

2.1 Literature Review

2.1.1 Plasma Background

In a basic chemistry class plasma is often introduced as the fourth state of matter. As the temperature of matter increases it changes phase from a solid to a liquid to a gas and finally to a plasma. A primary example of a plasma is stars, and specifically the sun. While plasma is the most common state of matter in the universe it is the least familiar state to humans. In order to understand plasma processing and plasma chemistry a more detailed definition is needed.

A plasma is group of charged particles that is quasineutral and exhibits a collective behavior [1]. As energy is added to molecules in a gas, the molecules become unable to store energy in vibrational, rotational, or translational modes and become ionized. For a plasma to be quasineutral it must have a net neutral charge. In a singly ionized plasma this means that the number of ions and the number of free electrons are the same. A plasma must also be large enough that the distance over which a charge disturbance can be felt, known as the Debye length, is much smaller than the total dimension of the plasma [1]. Collective behavior refers to the fact that molecules no longer have just forces due to collisions like in a gas. A plasma has enough charged particles that the motion of a single particle is determined not only by local conditions, but also by electric forces from particles far away in the plasma [1]. If an ionized gas exhibits these characteristics it is considered a plasma.

The two biggest categories of plasmas are thermal and non-thermal [2]. A plasma is considered thermal if the electron temperature is the same as the gas temperature. In this case the energy to ionize molecules comes from the high temperature of the gas and is on the order of 10000 Kelvin or greater. This is the most common form of plasma, and is the form of all naturally occurring plasma such as stars or lightning. A non-thermal plasma is manmade and is usually generated with an electric field. In this case the gas temperature remains low (around 300 Kelvin) while the electron temperature is around 10000 Kelvin. In this case the electric field is providing the energy for molecules to ionize and form a plasma. Another term often used to describe a plasma is equilibrium or non-equilibrium. This refers to the fact if the electronic, vibration, rotation, and translation temperatures are the same. This happens in a thermal plasma. A plasma is non-equilibrium when these temperatures are not the same which happens in a non-thermal plasma.

There are three main types of electrical DC plasma discharges: coronas, glows, and arcs. An example of these discharges along with their characteristic voltages and currents can be seen in Figure 1. A corona is a non-thermal discharge that tends to happen at atmospheric conditions. They are a low current discharge that requires a sharp gradient in electric field [3]. They are typically created by a needle or exposed wire tip. Because this type of plasma is non-thermal and low power it is a useful process for applications like wastewater treatment [4]. If the electric field strength continues to increase the main ionization process will change from background ionization to ionization from electron collisions. The latter, known as electron avalanche process, leads to exponential growth in the number of ions and electrons. The result is called a breakdown, and is the transition to the next form of electrical discharge, glow.

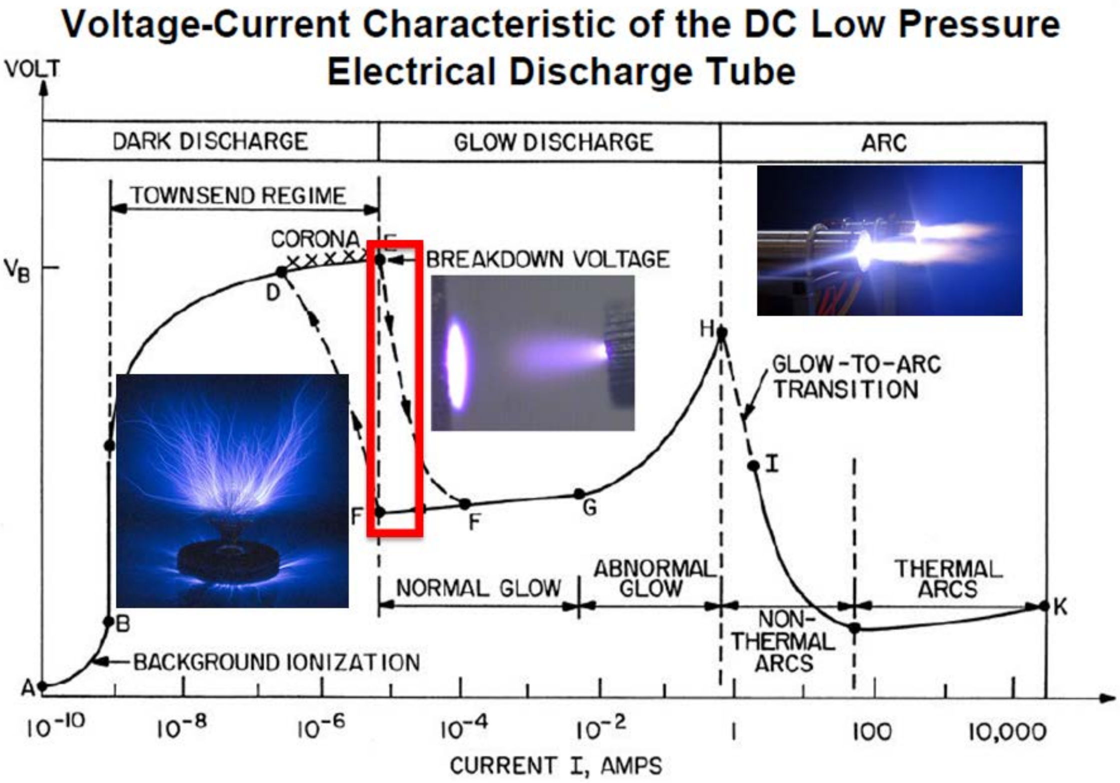


Figure 1 Voltage-Current characteristic for DC electrical discharge[5] showing examples of the 3 distinct discharge regions: corona[6], glow[7], and arc [8] with the red box highlighting the region in which a spark discharge will occur

A glow discharge is a low voltage and high current discharge that typically takes place at low pressure. A glow discharge is a non-equilibrium plasma most commonly used in lighting applications like fluorescent tube lights. They are also used in the semiconductor industry for deposition and etching. More recently atmospheric pressure glow discharges are being studied for materials processing applications without vacuum systems [9]. High pressure glow discharges have to be small in order to keep the breakdown voltage low since the breakdown voltage is dependent on pressure multiplied by distance. This is known as Paschen scaling [10]. The final transition is from glow to arc.

An arc is an even higher current discharge than a glow and tends to happen at atmospheric pressure. At this point the plasma temperature is very high and can be considered an equilibrium plasma. Arcs are generally used for welding or cutting metals because of their high temperature. These three different types of discharges all have very different properties and specific applications that go along with them. There are different variations of each of these types of discharges to provide an even more application specific discharge.

Another special property of a plasma is that it can be transient or steady state. All of the discharges previously discussed were steady state discharges. An arc is often a desirable discharge for plasma chemistry, however the high gas temperature is not ideal for most applications. By a capacitor in an external circuit, the amount of energy transferred by the discharge can be limited. When the transition to an arc occurs a large amount of current is passed through the discharge. Once the energy in the capacitor is all gone the discharge shuts off never actually reaching a steady state arc. This allows the gas temperature to remain relatively low but still allows the discharge to remain high power. This is known as a spark discharge. A spark plug in a car works in a similar fashion. The discharges used to process oil in this research are most accurately described as spark discharges. Another transient arc discharge called a gliding arc was developed for a similar application [11]. An arc travels along a diverging nozzle in a high speed air flow. This causes the arc to ignite travel along diverging electrodes and extinguish. Because the arc is moving it never reaches a hot steady state condition. One of the main advantages of a transient arc discharge is the combination of relatively high power input and low plasma temperature.

2.1.2 Microplasmas

An important new field in plasma research is the field of microplasmas. A microplasma is a plasma on a small scale with dimensions usually measured in micrometers. For high pressure, high density applications like glow discharges in atmosphere [9] or discharges in liquids [12], the discharge size must be small to create a stable discharge because of Paschen scaling or *pd* scaling. As the discharge pressure increases the discharge size must decrease for the discharge to remain stable and have the same breakdown voltage and operating regime which can be seen in Figure 2 [10]. In this way, *pd* acts as a non-dimensional number that can be related to the Knudsen number. For any given pressure there is a minimum breakdown voltage required for a discharge [13].

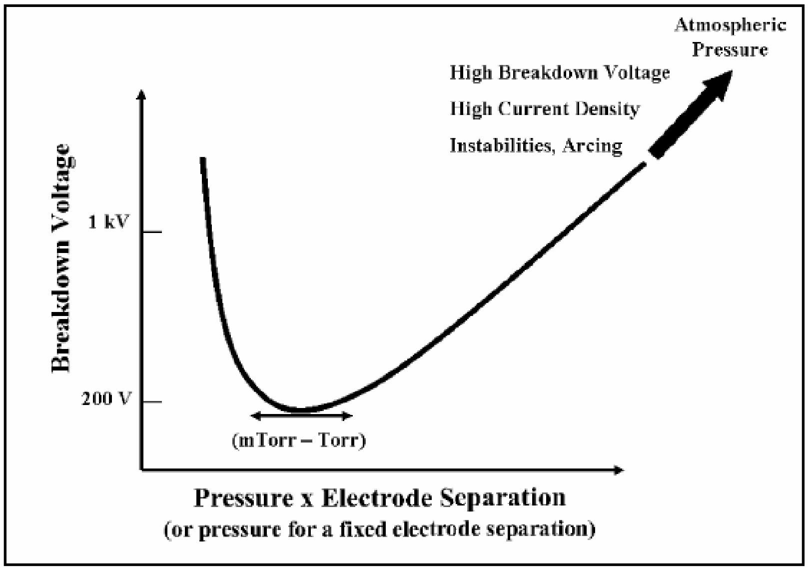


Figure 2 Schematic Paschen curve from Foest et al. [10]. The minima is generally around .5-5 cm-torr

An important application for microplasma is the fact that they can be used to selectively generate active species [10] and they have a very high power density [2]. Because high pressure leads to high charged particle densities in a plasma, and because of their small size microplasmas can have very high energy without having a high gas temperature. This important trait of microplasmas makes them ideal for plasma chemistry because they can create radicals without raising the temperature of the medium. The field of microplasmas is rapidly expanding with a wide range of applications ranging from using a dielectric barrier discharge to neutralize a VOC gas with the device shown in Figure 3, or biological applications such as sterilization of water [4] or wounds [14]. They have also been used for gas analysis to detect elements in an environment [15]. Another popular application is to use a microplasma create reactive species for chemical reactions in a reactor [14]. This also happens to be the application developed in the work done for this thesis.

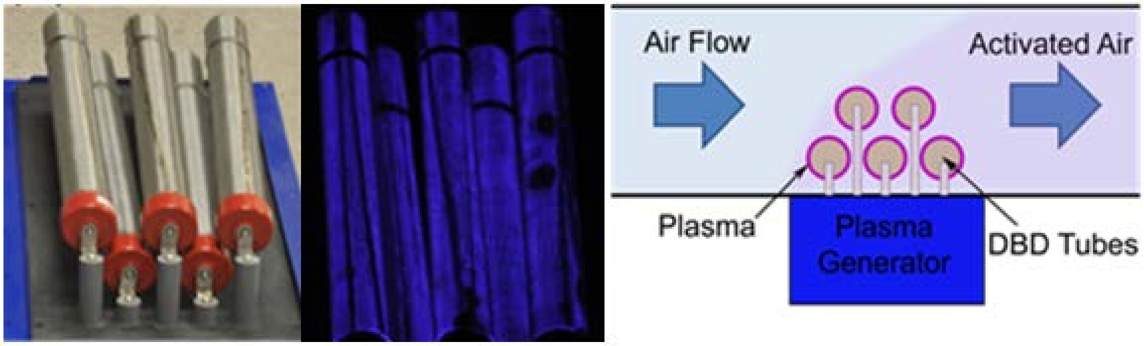


Figure 3 A tube DBD plasma generator used to create Oxygen and Nitrogen radicals in air in order to neutralize a VOC gas such as ethylene

2.1.3 Plasmas in Liquids

Plasmas in liquids are an important subject pertaining to high pressure microplasmas. This is an area of interest in order to apply plasma chemistry to molecules in the liquid state. A liquid has a much higher density than a gas giving it a lower electrical conductivity and making it more difficult to form a plasma. Because of this a much higher voltage is needed in order for breakdown to occur between two submerged electrodes. There is much debate over the exact mechanisms of breakdown in liquid [12]. Because of impurities in the liquid or dissolved substances it is difficult to predict exactly when breakdown will occur. The important part is that when a plasma is generated in a liquid, reactive species are created that can be used for other desired reactions [12]. The type of liquid, and other dissolved species will determine exactly what type of radicals are generated and what chemical reactions will occur.

Experiments have been done to water reform oils using similar mechanisms to the microplasma ball reactor. Water droplets replace the metal balls and with a high electric field in the fluid mixture a plasma discharge can be created between the water droplets and electrode through the oil as seen in Figure 4. This process is similar to steam reforming of heavy oils in order to upgrade them [16]. Water is used as a hydrogen donor in order to decrease the C/H ratio in the oil.

Figure 4 Plasma discharge in water and mineral oil mixture.

2.1.4 Plasma Chemistry

Understanding radical chemistry is an important step in understanding plasma chemistry. A radical is an atom or molecule with an unpaired electron [17]. It is generally an intermediate product in a chemical reaction that lasts for only a brief period of time. Radicals are unstable because of their unpaired electron and generally react again quickly. Some common radicals are CH_3, OH, H, and other general hydrocarbon radicals. If there is a way to create radicals in a non-energy intensive way, the radicals will react easily afterwards so that the total reaction chain energy cost is relatively low. Radicals can also initiate chain reactions making them an incredibly important factor for liquid hydrocarbon processing. Table 1 shows an example of possible radical induced reactions [18]. In reality there are hundreds of these reactions all happening simultaneously.

Table 1 Possible reaction pathways for hydrocarbon radical chemistry [18] induced by electrons from a plasma

Initiation	$e^- + CH_3CH_3 \rightarrow 2\ CH_3\bullet + e^-$
Initiation	$e^- + CH_3CH_3 \rightarrow CH_3CH_2\bullet + H\bullet + e^-$
Propagation – Hydrogen Abstraction	$CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\bullet$
Propagation – Decomposition	$CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + H\bullet$
Propagation – Polymerization	$CH_3CH_2\bullet + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\bullet$
Termination – Hydrogenation	$CH_3\bullet + H\bullet \rightarrow CH_4$
Termination – Recombination	$CH_3\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_3$
Termination - Disproportionation	$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + CH_3CH_3$

The three main types of reactions are: initiation reactions to form radicals, propagation to maintain the number of radicals available for reactions, and termination to end the chain reactions through recombination of radicals [19]. In order to initiate the formation of radicals, an energetic third body must collide with a hydrocarbon. In the case of a plasma, free electrons are generally the third body. The addition of hydrogen as a donor will lead to the creation of hydrogen radicals and hydrogenation to decrease the overall C/H ratio. While the above list of reactions is by no means a complete one, it serves to illustrate the type of reactions that will take place in plasma processing of hydrocarbons.

Plasma chemistry involves using the unique features and characteristics of a plasma to facilitate chemical reactions more efficiently than by thermal means. Plasmas generate charged particles, excited species, free radicals and photons which can all be used to facilitate chemical reactions [2]. In general, non-thermal and non-equilibrium plasmas are used for chemistry because they are lower energy and avoid heating up the surrounding environment. Because of this radicals can be generated at low temperature preventing other potentially unwanted thermally driven reactions such as pyrolysis or soot formation. In order to overcome activation energy of a reaction, traditional catalysts are used. These are often expensive and can be poisoned and must be replaced [20]. The species generated by a plasma are energetic and can often overcome the activation energy of a reaction by themselves. This is known as plasma catalysis. This makes plasma catalysts much easier to work with and more efficient than traditional catalysts.

The radicals generated by a non-equilibrium plasma can be used for many applications. Plasma catalysis for fuel conversion involves using generated radicals to break up or “crack” liquid hydrocarbons. Vehicle on board fuel conversion is useful for fuel cell applications [21]. Work has been done to convert octane into hydrogen by different non-equilibrium discharges such as a corona [22],a gliding arc [23], or another form of low current arc [24]. Plasma catalysis is also useful for synthesis reactions. Work has been done using a dielectric barrier discharge to convert methane to syngas and liquid hydrocarbons [25]. A dielectric barrier discharge in carbon monoxide can be used to make the carbon suboxide polymer [20].

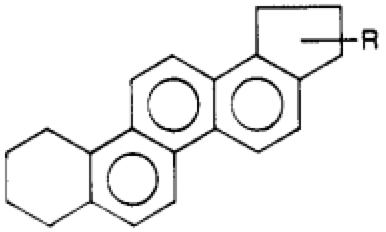
Of particular interest to this research is the generation of radicals in liquid hydrocarbons in order to promote cracking reactions. A microplasma spark is a transient non-thermal and non-equilibrium discharge is the plasma used in the reactor for this application. The microplasma spark is a DC electrical discharge and is located in the transition region between a corona and a glow discharge and is highlighted by the red box in Figure 1. The discharge has a high power density to rapidly produce radicals, but the size is small in order to keep the temperature of the fuel low. The microplasma in liquid generated by the ball reactor is unique because of its ability to generate non-equilibrium plasmas in liquid. In contrast, most reactors creating discharges in liquids lead to thermal chemistry [21]. The details of the reactor design will be described in a later section.

2.1.5 Oil and Fuel Composition

There are two main types of liquid hydrocarbons on which experiments were performed. JP-8 and heavy crude oils can both benefit from plasma processing, but in slightly different ways. The goal is to turn JP-8 into propane like fuel. The goal for the heavy oils is to convert them into lighter liquid hydrocarbons in order to lower the viscosity. Both fuels will go through cracking reactions with the objective being to reduce the average chain length of hydrocarbons.

Jet Propellant 8, also known as JP-8 or NATO F-34, is jet fuel used by the military in tanks and planes [26]. It is a kerosene based fuel with additives that reduce the freezing temperature increase the flash point, and reduce corrosion among other things [26, 27]. JP-8 has higher sulfur content than traditional fuels like gasoline or diesel. These characteristics make the fuel safe, reliable, and cost effective for use by the military. For safety reasons it is the only fuel allowed to be transported by the military which makes the ability to convert JP-8 into another type of fuel easily at a specific location ideal. This is known as forward operating point flexibility.

Heavy oils are a non-conventional energy source that is rapidly becoming more economically viable. These oils are high density; in fact their density is very close to that of water. This is a trait common to immature or degraded oils [28]. While it is logical to think that these oils are composed mainly of high molecular weight long chain hydrocarbons, this is not correct. There is in fact a distribution of a wide range of molecular weights [29]. There is a mix of both long and short chain hydrocarbons as well as complex ring structures like the one seen in Figure 5. One thing that does have an impact on oil density is the carbon to hydrogen ratio (C/H). As the C/H ratio increases the density of oils also increases [28].



C_nH_{2n-22}

$R = H$ m/z 272
$R = C_5H_{11}$ m/z 342
$R = C_{10}H_{21}$ m/z 412
...
$R = C_{50}H_{101}$ m/z 972

Figure 5 Example complex hydrocarbon found in heavy oil [30]

Even though heavy oils are not as valuable as light oils, there are many refinery processes to extract usable energy from them because they are so plentiful. There are different desulfurization or demetalation techniques along with hydrocracking and distillation processes [28]. Distillation involves boiling of the oil in order to separate the light and heavy portions of the oil, with the light portions being the usable and desirable portions. After the oil is put through an atmospheric distillation column and then a vacuum distillation column only the heavy tar is left over, which is known as the vacuum residual. Hydrocracking involves cracking the molecules in the oil breaking the carbon bonds in the large chains making lighter products by the addition of hydrogen to decrease the overall C/H ratio. While hydrocracking is valuable to convert something not useful into something that is, it is a very energy intensive process requiring high heat and pressure. Even so, there is an upper limit on the temperature at which existing technology works. For very heavy crude oils, a significant fraction is not able to be processed. Alternative methods of refining heavy oils are a valuable asset to making heavy oils an economically feasible alternative energy source.

2.1.6 Related Work

Using plasma chemistry to reform hydrocarbons is not a new field. Work has been done to convert all types of liquid fuels into hydrogen gas [21]. One popular devise for fuel conversion is a plasmatron which is a reactor that creates a low voltage high current thermal plasma arc. A mixture of air and hydrocarbon is fed into the reactor and exposed to the plasma where the hydrocarbon is broken down to create hydrogen [31]. The devise has been used to convert methane [31, 32] and diesel fuel [33] into hydrogen gas for fuel cell applications.

Another hydrocarbon reforming technology is a gliding arc discharge. In this type of reactor, a fuel air mixture is blown through diverging electrodes. An arc discharge ignites at the smallest part of the electrode gap, and as air is blown over the arc it travels down the diverging electrodes getting larger until it is eventually extinguished [34]. This method makes an arc discharge which is typically a thermal discharge, but makes it non-thermal. Because the arc is traveling along the electrodes it is constantly in a transient state. The air molecules never get a chance to heat up but the reactive species are still created. This allows the process to be more energy efficient. This technology has been used to reform different liquid fuels such as gasoline, diesel, and JP-8 and convert them to syngas to be used as a technique for on board vehicle fuel conversion for hydrogen fuel cells [34-36] .

There has also been work done with hydrocarbon synthesis. A dielectric barrier discharge plasma is created in an annular gap between an outer metal tube and an inner dielectric tube. A feed gas of methane and carbon dioxide was used to synthesize liquid hydrocarbons [25, 37].This is important because it illustrates that based on how a plasma discharge is controlled, the plasma chemistry reactions can be fine-tuned to a specific application.

While these technologies all use plasma chemistry to convert a hydrocarbon fuel into a useful product none of these are exactly what is needed for converting JP-8 into propane or reforming heavy crude oil. The closest technology to the microplasma ball reactor is work done using metal chips submerged in oil. When two electrodes are submerged with a high voltage difference, plasma sparks are generated between the metal chips [38]. In this case hydrogen gas is the main product, but methane and other higher products are also produced in small amounts. The objective of the microplasma ball reactor is to not totally break apart the hydrocarbon into just hydrogen gas, but to slightly reduce the average hydrocarbon chain length.

2.2 Ball Reactor

The microplasma ball reactor was originally studied using JP-8. The purpose of this reactor is to convert JP-8 into propane for UAVs or cooking stoves. The problem with all of the previous methods of fuel conversion is that the hydrocarbon molecules get completely destroyed creating hydrogen gas as a product. The microplasma ball reactor was created as a way to limit the energy in the plasma and maintain non-equilibrium plasma chemistry. A small plasma will generate enough radicals to break carbon bonds but the plasma doesn't have enough energy to drive thermal reactions and completely break up the molecule. The motivation for creating a reactor for crude oil is similar. The goals are to find a way to economically refine vacuum residual in a refinery setting, and also to create a field process that can reduce the viscosity of oil at the well site to make pumping more efficient.

In order for the microplasma ball reactor to be useful and efficient it must have a high total power input, but it must also deliver that power in small energy pulses as microplasma discharges in order to get the desired chemistry. In the reactor, a small metal ball is placed in between two parallel high voltage electrodes as seen in Figure 6. Whichever electrode the ball is originally in contact with is the charge the ball originally has. The ball then acts like a charged particle in a DC electric field and is accelerated toward the opposite electrode. As the ball approaches the opposite electrode a small microplasma discharge occurs as charge is transferred from the ball to the electrode or from the electrode to the ball. Now that the ball has the opposite charge it is accelerated back in the direction it came. The microplasma discharge is visible in frame number four.

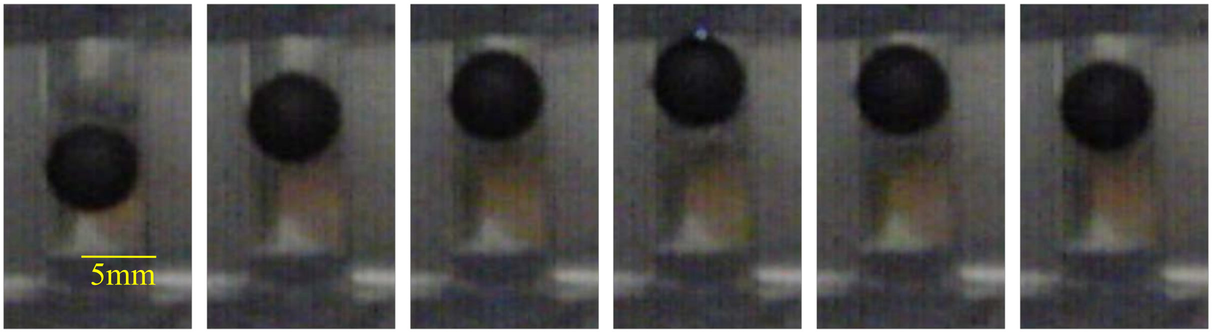


Figure 6 Storyboard of ball bouncing between high voltage electrodes in mineral oil

The ball setup allows both for potential high total power input, and keeps the discharge size small. The capacitance of the ball, given by the following formula based on the ball size and electric field [39], limits the amount of total charge that can be stored and therefore the amount of energy in the discharge.

$$q = \beta k \varepsilon_0 d^2 E_0 \tag{1}$$

β is a field enhancement factor, k is the dielectric constant of the medium, and ε_0 is the vacuum permittivity [39]. Not only is the energy in this discharge small, but it is also consistent with each discharge because the same amount of charge is transferred with each bounce. This allows for very fine tuning of the energy released in a discharge by changing the capacitance of the ball. Because of the rapid bouncing of the ball, the discharges happen rapidly to maintain a relatively high total power. Because the balls are small a large number can be packed into a small area to increase the power density. These characteristics make the microplasma ball reactor ideal for both the JP-8 and crude oil applications.

The reactor was designed in order to efficiently pack the metal balls. As previously mentioned, the original reactor was designed to run in JP-8. The structure of the reactor was created using nylon from a 3D printer and can be seen in Figure 7. Rigid columns were used with a single ball per column with each column vertically separated by wire electrodes. Keeping the balls separate allows for greater control of the size and timing of the discharge as opposed to many balls bouncing around an open chamber. Wire electrodes are used in order to reduce leakage current through the oil as well as let fluid flow more freely through the columns. Since the desired product, propane, is a gas it needs a way to escape the reactor.

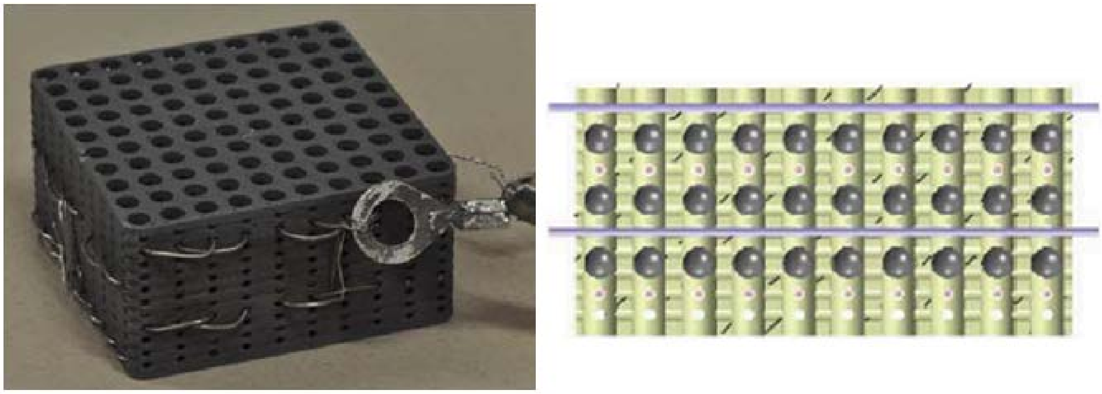


Figure 7 Picture and CAD drawing of ball reactor

The other aspect of the reactor is the ball size and material along with the electrode gap spacing. An extensive study was done that will be detailed later on the gap spacing and ball size. The important scaling parameter is the length to diameter ratio or the L/D ratio. It is important that the gap is large enough so that a breakdown does not occur across the whole gap, but the gap must be small enough that the viscous losses as the ball moves through the fluid don’t hinder the efficiency. The material of the balls was chosen so that the electrostatic force required to move them would not be too great as to hinder the efficiency.

When converting the JP-8 reactor to a heavy oil reactor some difficulties were encountered. The first set of difficulties comes from the properties of the oil. Heavy crude oils are very viscous making them difficult or even impossible to work with at room temperature. Since one of the most important aspects of the microplasma ball reactor is the bouncing aspect of the metal ball, a high viscosity fluid will hinder the ability of the ball to move. Another problem with high viscosity oils is that whenever the plasma discharge happens, a gas bubble is created it becomes trapped very easily. Trapped gas leads to a plasma discharge happening in the gas which is an inefficient and more thermal discharge than the microspark discharge. Because the electrical conductivity of gas is higher than liquid a discharge that crosses the entire gap is more likely to occur. Some ways to decrease heavy oil viscosity are to mix the heavy oil with a lighter one or to heat the oil. The latter can pose additional problems.

Another difficult property of heavy oil is its conductivity due to dissolved metals in the oil. Because the plasma in the reactor is generated by electricity this can pose a big problem. When the oil is conductive, current travels not only by the plasma discharge between the ball and the electrode, but current will travel from electrode to electrode through the oil slowly. This leakage current will resistively heat the oil. While heating the oil makes it less viscous, it also makes it more conductive. This leakage current can prove to be a major inefficiency in the processing of the oil. There is a tradeoff between high conductivity and high viscosity when it comes to choosing the oil processing temperature.

Another problem also partly due to running the process at high temperature is that light hydrocarbons evaporate and are lost. This problem is really only an issue for the heavy crude oil because with the JP-8, it is desirable to make a gaseous product. In general more light hydrocarbons will escape at a higher temperature. In addition to heating the oil, the plasma discharge will locally vaporize some of the liquid hydrocarbons. It would be ideal if these light hydrocarbons would stay in the liquid phase and be available for recombination. In order to prevent these light hydrocarbon losses the reactor process was done at an elevated pressure.

A pressure vessel was used in order to run the microplasma ball reactor at high pressure and temperature. This allows processing to occur at high temperature order to reduce the viscosity while there is high pressure as well as prevent the loss of light hydrocarbons. The light hydrocarbons and radicals generated by the plasma are kept more in the liquid phase making them available for recombination. The use of a pressure vessel also allows for a gas phase hydrogen donor. Experiments were done with bubbling hydrogen and methane through the oil in order to dissolve a hydrogen rich gas in the oil instead of using liquid phase oil with a lower C/H ratio than the crude oil as the donor of hydrogen. Being able to run the cracking process as high pressure is an important step in creating a working process.

One of the issues with running experiments at high pressure is that undesirable gasses may become dissolved in the oil. These gasses may actually displace other dissolved gasses and increase the viscosity which is an undesirable outcome. The other issue is that having the experimental setup inside of a pressure vessel prevents changes from being made while the experiment is running and can make diagnostics of what is going on difficult. The pressure vessel is one of the most important pieces of equipment in the process of cracking heavy oil with the microplasma ball reactor, but it does introduce a new set of problems.

3. EXPERIMENTAL SETUP

3.1 Electrical Circuit Configuration

One of the most important parts about plasma generation is the circuit used. Experiments were done with one ball or even different configurations of microplasma ball reactors, but the electrical setup is generally similar. A schematic of the system is shown below in Figure 8. The power supply used was a Spellman SL300 high voltage power supply. It can generate between 0 and +40 kV and up to 7.75 mA. The high voltage is necessary to create a strong electric field for the plasma, and low current generation is fine because the plasma is relatively low energy. A ballast resistor was used in series with the plasma in order to protect the power supply. Generally a resister on the order of a megaohm was used. The resistor prevents the plasma from drawing too much current too fast from the power supply. For different experiments a microplasma ball reactors with all different number and types of balls were used interchangeably. Lastly, a Fluke digital multimeter was used in the circuit in a few experiments as a diagnostic tool to monitor the current pulses from the plasma generated from the bouncing ball. Whenever a multimeter was not used, the ball reactor was connected directly to ground along with the power supply.

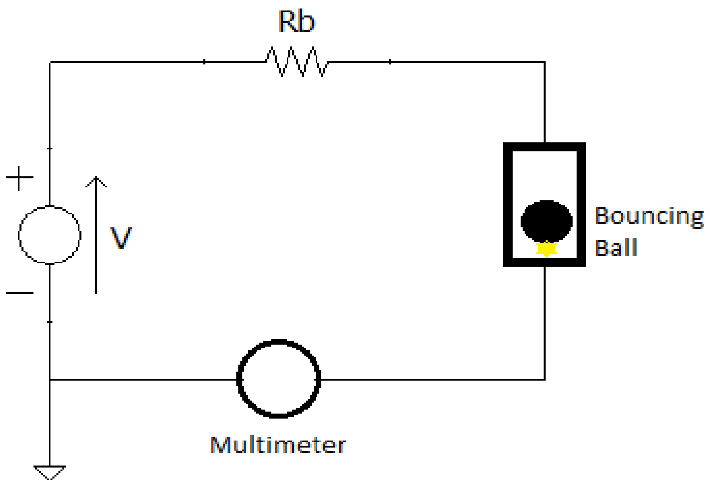


Figure 8 Circuit diagram of microplasma ball reactor setup

3.2 Reactor Geometries

3.2.1 Nylon Reactor

Throughout the experiments performed, the geometry of the reactor changed dramatically. The first experiments were done using a single ball setup. In order to optimize the current density and ultimately the power dissipated by the plasma, the bounce frequency was maximized. This was done by testing different ball sizes, and material densities along with column length and maximum voltage before breakdown. The ball was trapped in a plastic tube with one stationary electrode and one screw tip for the other electrode that was adjustable. From these experiments the optimum column length, ball diameter, and ball density were determined.

From the data gathered from the ball frequency optimization experiments detailed in chapter 4, a 300 ball reactor was designed for use converting JP-8. This is the reactor that was shown in a previous section in Figure 7. The reactor was designed in

Solidworks and then printed on a 3D printer using a nylon material. The reactor was 2 inches wide and long and 1 inch tall. 1/8 inch steel metal balls were placed in 100 evenly spaced columns stacked three balls to a column. The balls in each column were separated by .038 inch stainless steel wire that alternate on either side of the ball between being a high voltage electrode or a ground electrode. The reactor acts like 300 individual columns all discharging in parallel so that each column and plasma discharge is identical.

For the JP-8 experiments the reactor was placed inside of a sealed chamber and submerged in JP-8 as seen in Figure 9. The sealed vessel was made out of nylon and was sealed by a rubber gasket and see through acrylic lid that was held down by 8 nylon screws. Two electrical feed throughs were created to be attached to the wires on the reactor acting as either ground or high voltage electrodes. A gas opening with a compression fitting was made so that a syringe can be attached to capture gas produced be the reactor so that it can be analyzed later.

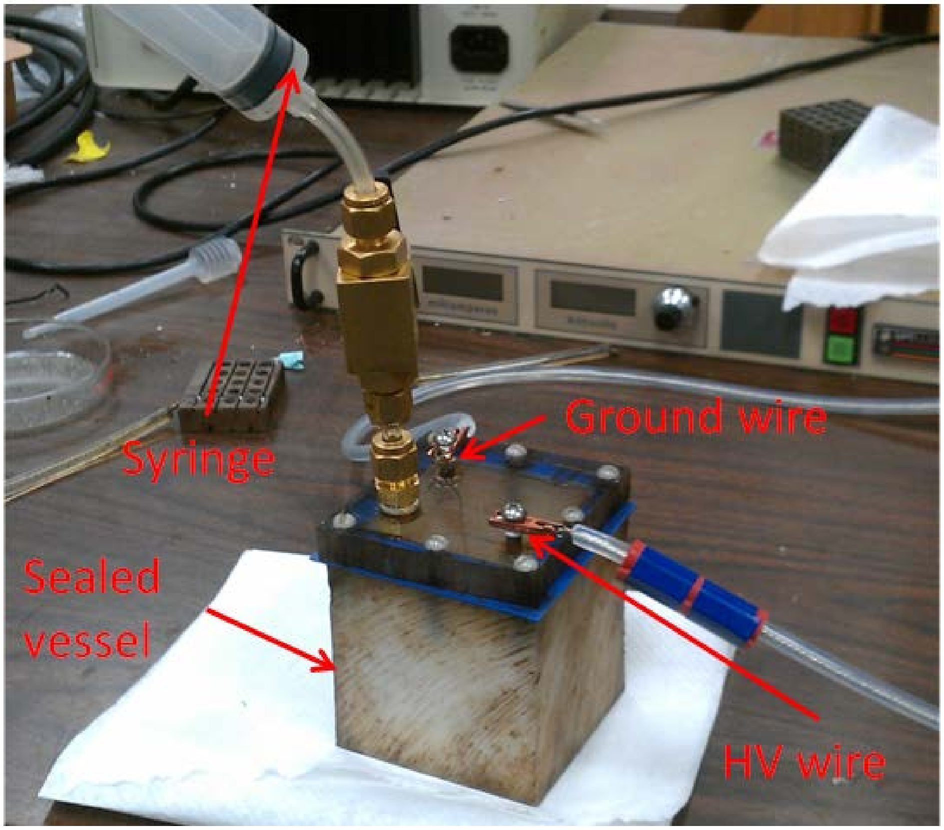


Figure 9 Sealed reactor setup for JP-8 microplasma ball reactor

3.2.2 Ceramic Reactor

When designing a microplasma ball reactor to work for reforming heavy crude oil, a couple of different designs were considered. First the setup pictured above was used with the exception of no syringe was used to capture gas, and a hot plate was used to heat the oil. Because the columns were so small and the oil so viscous it did not work. A new reactor was designed in Solidworks that used ¼ inch aluminum balls instead. The reactor was the exact same overall size; the only difference was the number and size of the columns. The above setup with this new reactor worked to some degree. Problems arose because the reactor would partially melt and deform because of the heat required for processing, and many hydrocarbons were lost in the gas phase leading to inefficient processing. Because of this it was decided to change the material of the reactor to a more durable ceramic.

A ceramic reactor was used for experiments with heavy crude oil reforming at high temperature and pressure. A low cost machinable alumina silicate ceramic was bought from Cotronics Corporation. Once again the reactor geometry was designed in Solidworks, but it was then sent off to get machined in a CNC machine at a local machine shop. While the ceramic is in the machinable form it does not have the electrical properties necessary for use in the microplasma ball reactor. After the part was machined it was then heat treated in a furnace. The part was heated to 1050° C at a rate of 90° C per hour. The part was held at 1050° C for 2 hours and was then cooled down over a period of 4 hours. This was done in accordance with the instructions provided by Cotronics about the ceramic that was purchased. A picture of the reactor after firing can be seen in Figure 10 and photos of the reactor running with the plasma discharges visible can be seen in Figure 11 and Figure 12. The reactor is 6 inches in diameter and ½ inch think. There are 163 columns in this reactor. Hollow aluminum balls that were ¼ inch diameter were used in order to allow the balls to move easily. The balls were held in with a copper wire that fits into the grooves with one side being the high voltage electrode and the other the ground electrode. Once again, many of the attributes of the reactor were based on experiment results detailed in chapter 4.

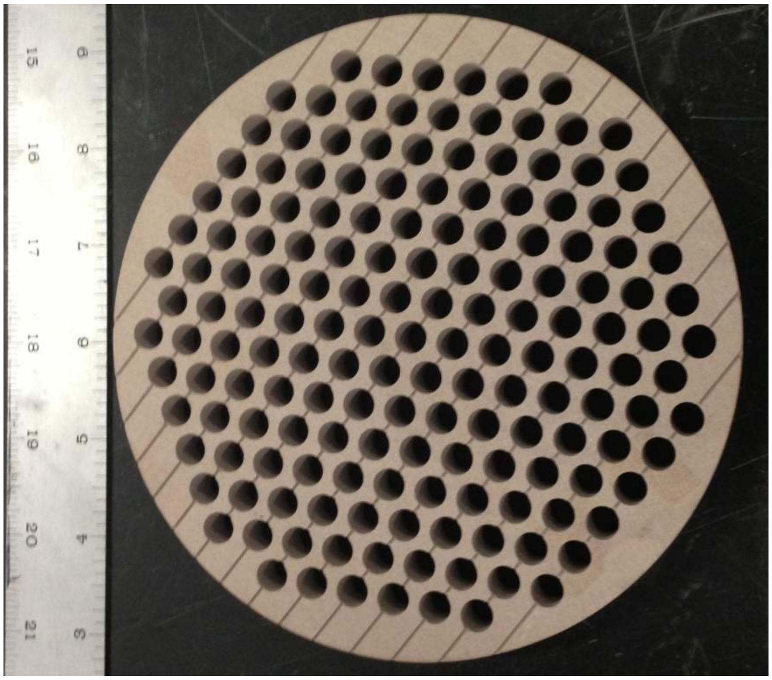


Figure 10 Ceramic ball reactor after machining and firing

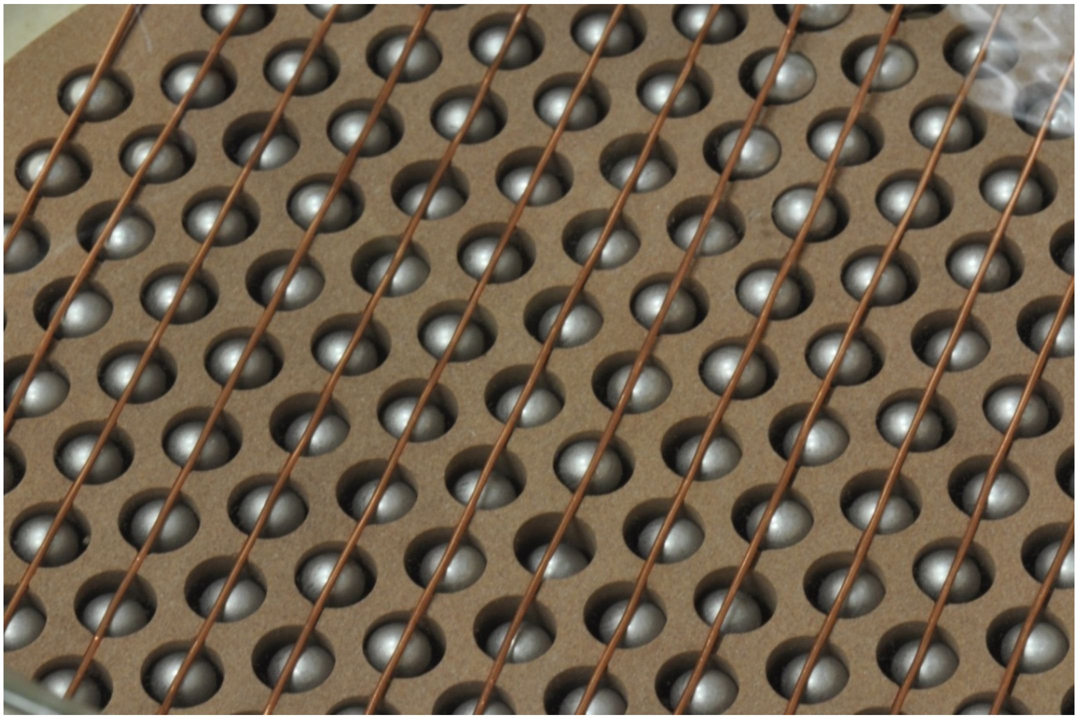


Figure 11 Picture of ceramic ball reactor running in mineral oil with lights on

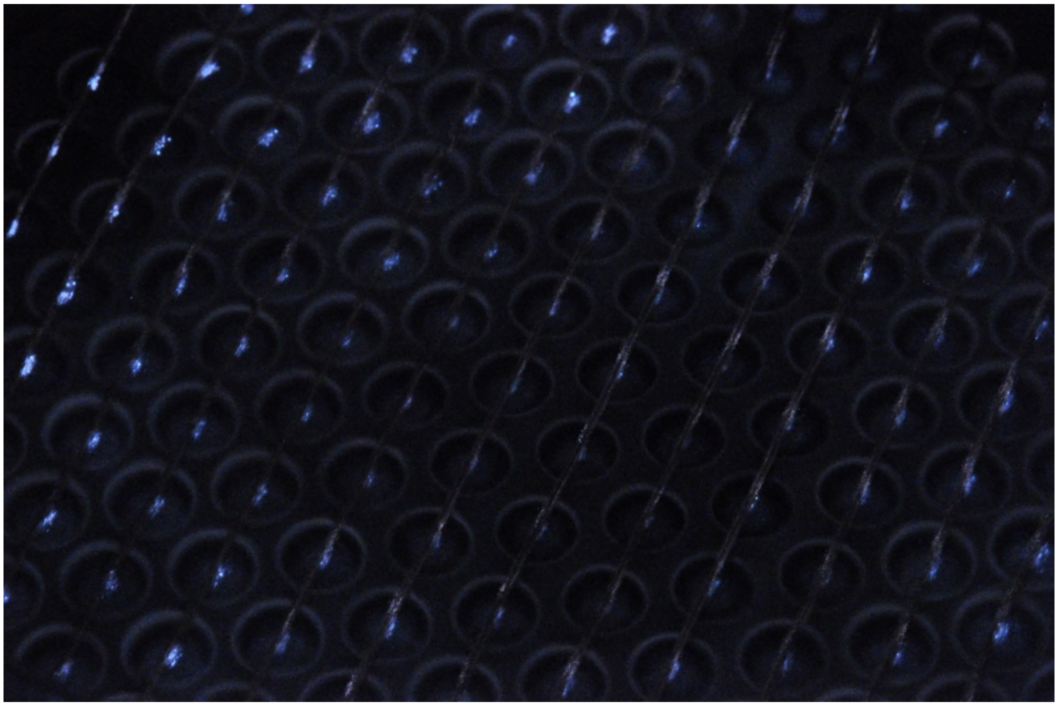


Figure 12 Picture of ceramic ball reactor running in mineral oil with lights off

3.2.3 Pressure Vessel

The ceramic reactor allows experiments with the microplasma ball reactor to be run at high temperature and pressure. In order to achieve both of these things a pressure vessel was introduced which can be seen in Figure 13 Picture of pressure vessel setupFigure 13 and Figure 14. The vessel is capable of holding up to 1500 psig, and is filled using cylinders of compressed nitrogen gas because it is inert and inexpensive. In the back of the vessel there is a ball valve which leads to a PVC exhaust line that is used for emptying the vessel. Inside the vessel there are five 500 W heaters that are controlled by a PID temperature controller and a high current relay which is controlled by a thermocouple submerged in the oil. The actual reactor is placed in a borosilicate glass pot which contains all of the oil being processed.

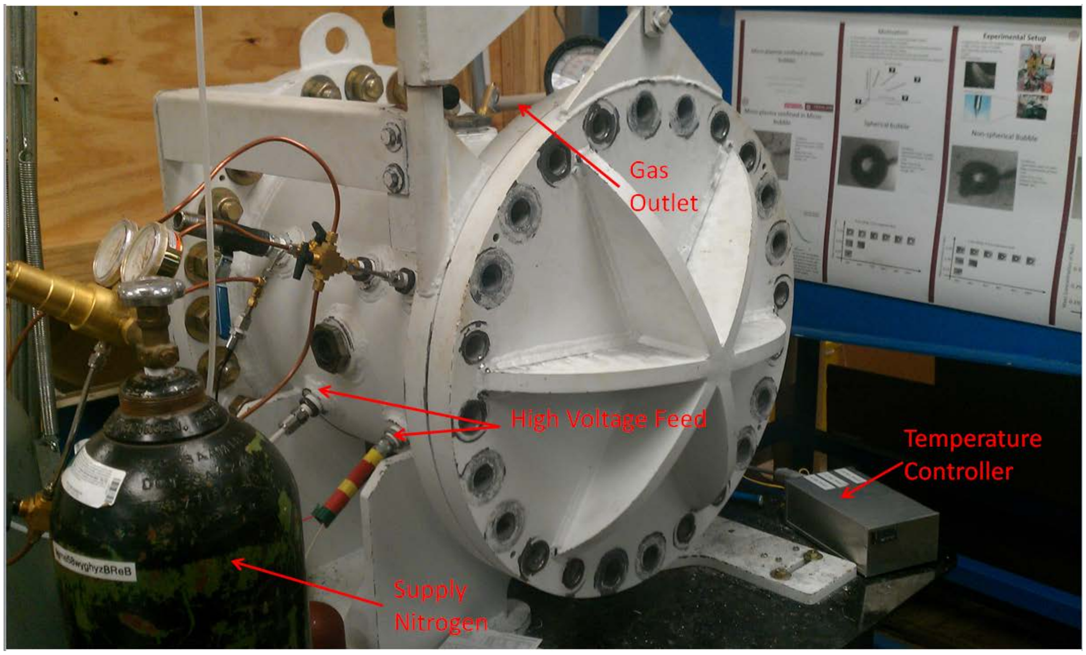


Figure 13 Picture of pressure vessel setup for running oil processing experiments at elevated temperature and pressure

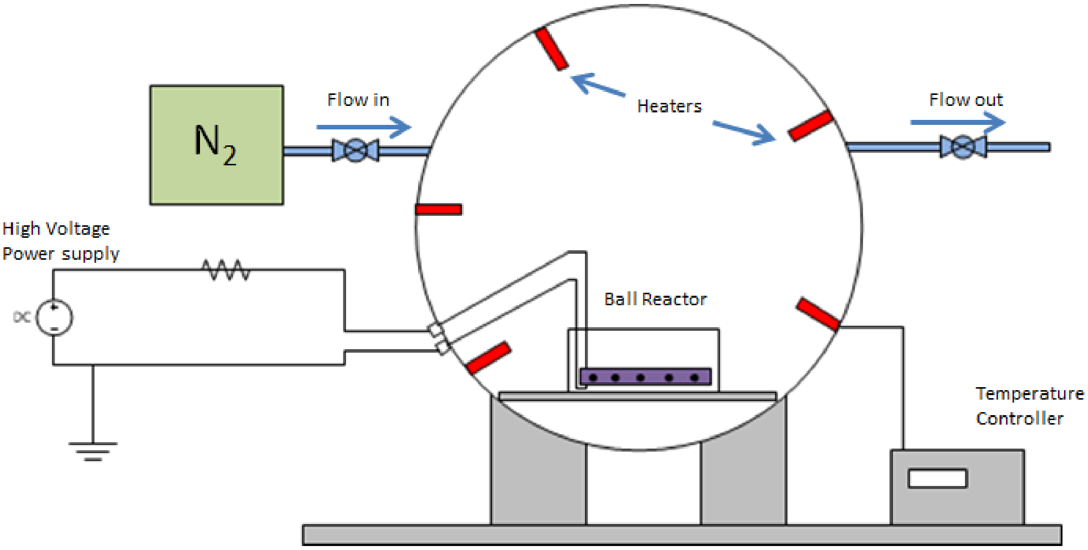


Figure 14 Schematic of pressure vessel setup

A few experiments were done using a gas phase hydrogen donor. A glass bubbler was used in place of a bowl to hold the oil and reactor. The bubbler has a piece of fritted glass on the bottom with fine enough holes so that gas and not liquid can pass through. Methane was blown up from the bottom and bubbled through the reactor and oil while the processing was taking place. There was difficulty getting the bubbler to work properly as seen in Figure 15. The oil had to be viscous enough that it did not flow back through the fritted glass, but it had to have a low enough viscosity so that methane could be bubbled through it. Because of safety regulations, methane was not allowed to be bubbled through at high pressure, and since high pressure was desired these experiments were soon abandoned.

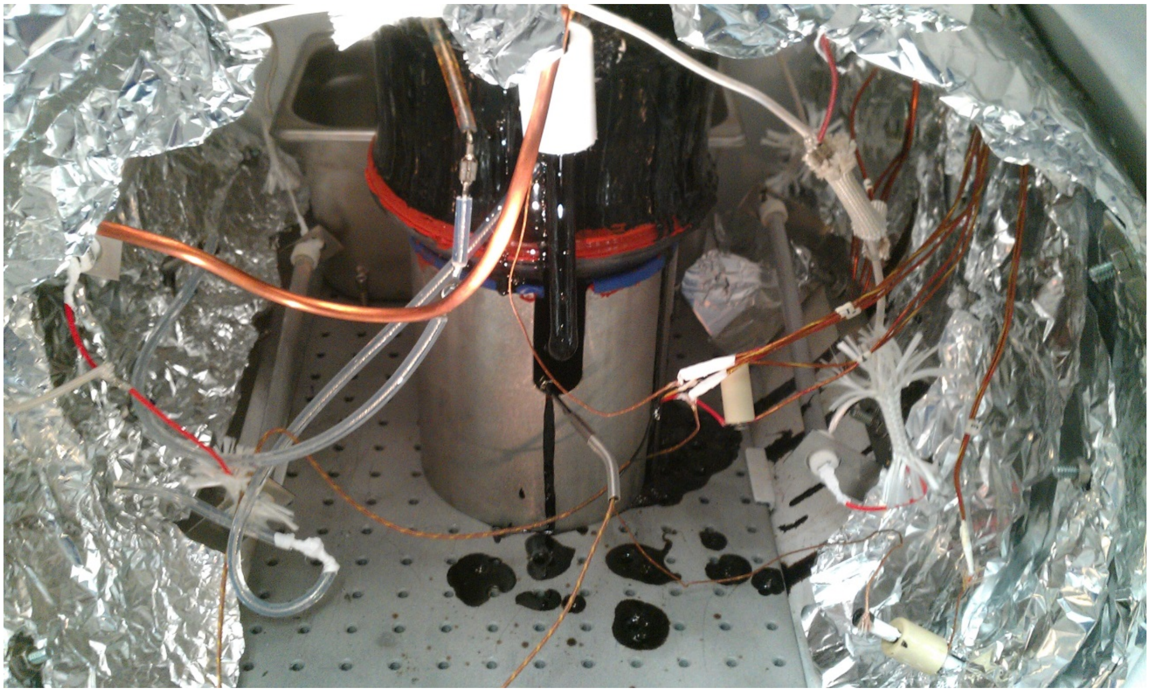


Figure 15 Bubbler in the pressure vessel after an attempt at bubbling methane through heavy crude oil

3.3 Diagnostics

3.3.1 Circuit Diagnostics

One of the vital pieces of information in experiments with the microplasma ball reactor is the power dissipated in the discharge which is the input energy in the reforming process. For the case of a single ball, the charge stored on the ball can be calculated. Using the digital multimeter, the bounce frequency was measured in order to determine the current and power. For both the nylon and ceramic microplasma ball reactors a different method was used. The power supply was hooked up to a Labview program that measures current and voltage.

The Spellman high voltage power supply generates separate signals for both the current and voltage output. The output is a 0-10V signal based on the range of the power supply output. From this the signal is read by Labview and multiplied by a constant to obtain the appropriate values for current and voltage generated by the power supply. Because there is a ballast resistor in the circuit (see again Figure 8 or Figure 14) the voltage generated by the power supply is not the voltage drop across the plasma. Using the known value of the ballast resistor and measuring the current through the system, the voltage drop across the resistor is determined by Ohm's law and subtracted from the measured voltage to obtain the voltage drop across the plasma. The plasma voltage and current were graphed in order to obtain a characteristic behavior for the microplasma reactor operating in different modes. An example voltage current relationship is given in Figure 16. Labview logs the current and voltage data with time as well as the power data which is determined by multiplying the voltage and current together. Labview also integrates power over time to determine cumulative energy input. Whenever experiments were done based on a specific energy input the Labview integration method was used to determine the total input energy.

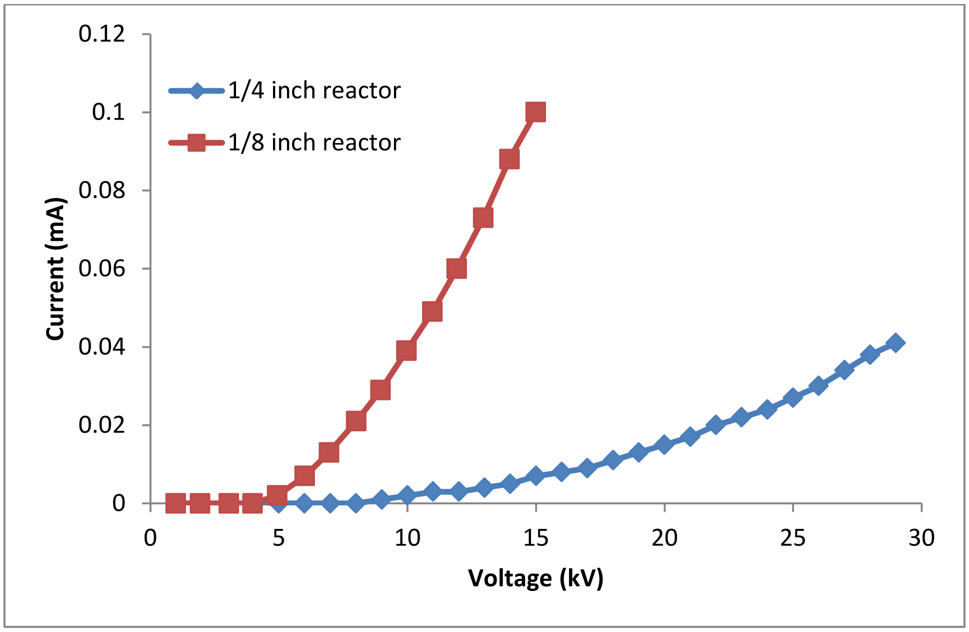


Figure 16 V-I relationship for the 1/4 inch and 1/8 inch nylon reactors in mineral oil

The above voltage current relationship has some specific features. First, the relationship is initially linear. Whenever there is not a high enough voltage for a plasma to be generated, the only way charge is transferred is by conduction through the liquid medium. Since mineral oil has almost zero conductivity as seen in Figure 16, this region of the graph appears flat. For the heavy oil mixtures with a higher conductivity this region is not flat. The second feature is the exponential relationship between voltage and current once the balls start to bounce and a microplasma is generated. This is the area of the curve that it is desired to process hydrocarbons in. The final aspect of the voltage current relationship is that once a breakdown occurs in the column the voltage will drop off rapidly while the current continues to increase. This is the region where the plasma is attempting to transition to a glow or arc discharge. The actual values of the current and voltage change with the reactor and oil type, but the general form remains the same.

3.3.2 JP-8 Diagnostics

In the experiments with JP-8 the objective was to create a gaseous product. The main diagnostic tools used were to analyze gasses. However, there was a soot produced in the JP-8 reforming process that also was analyzed. In order to figure out how much soot was being produced, it was filtered out and weighed after each run. Filter paper was weighed before having any product filtered over it. After a run in the JP-8 the remaining fuel was washed over the filter paper and the liquid was sucked through by a vacuum to catch the solid product. When the filtered product was completely dried it was weighed again to determine the total mass of the produced soot.

In order to analyze the produced gas, the produced samples were run through a gas chromatograph (GC) and mass spectrometer (MS) setup as seen in Figure 17. But first, in order to measure the gas flow rate, the time it took to fill the syringe to 35 ml during processing was recorded along with the voltage and current of the reactor. The filled syringe was injected into an SRI 8610C Gas Chromatograph with a thermal conductivity detector (TCD) and helium ionization detector (HID). Peak Simple software was used to run the GC oven and record the detector results. In order to use the GC to get the percent concentrations of different gas components it first had to be calibrated.

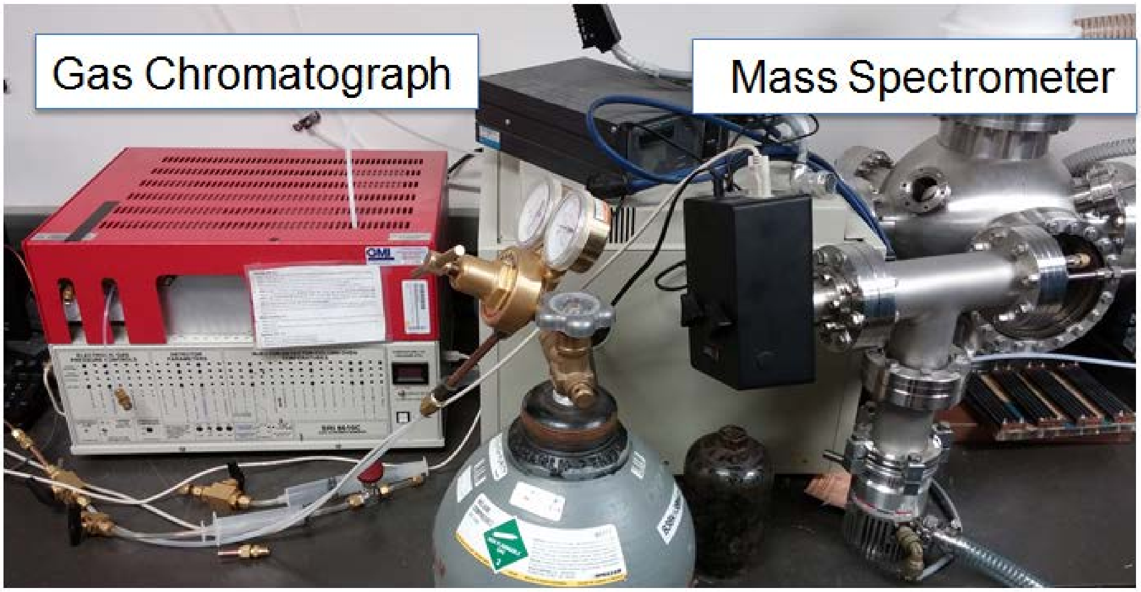


Figure 17 Picture of GC and MS setup used for gas species and composition analysis of gas produced during JP-8 processing

In order to calibrate the GC for hydrocarbon gas components a special calibration gas was used. This gas has a known composition of different hydrocarbons up through C_3 hydrocarbons. By measuring the relative peak area for known concentrations, a calibration constant for each gas component was determined. By assuming a linear relationship between peak area and relative concentration, the composition of the product from the JP-8 microplasma ball reactor was determined for different cases. The only problem with the GC is that it cannot determine what a specific gas component is in a mixture.

In order to identify the different components and peaks on the GC, a MS was used. The outlet of the HID on the GC was fed into a vacuum chamber with an Extorr mass spectrometer inside. A Varian S010 turbomolecular pump was used to evacuate the chamber. The ExTorr Mass Spectrometer came with a computer program that reads the ionization spectrum of whatever gas is inside the chamber. Because each molecule has its own unique ionization spectrum it was able to be determined what component each peak on the GC represented. After identifying each species the peak locations were mapped out as seen in the GC trace in Figure 18.

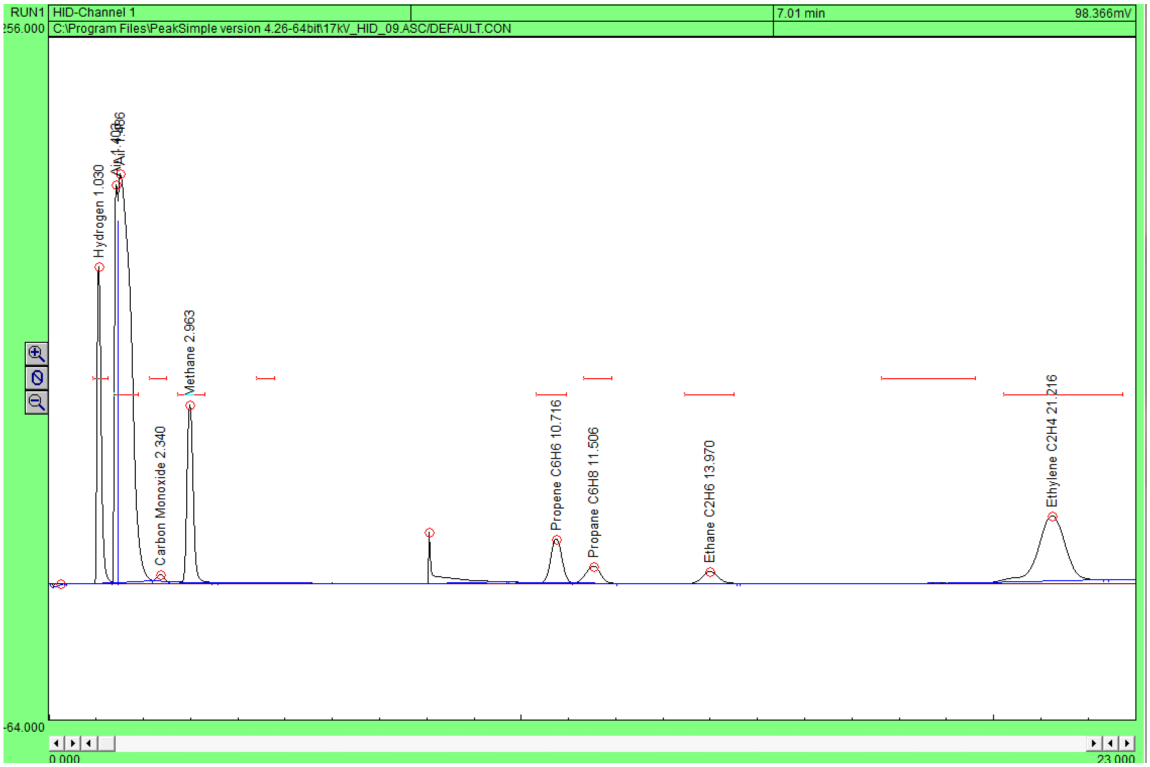


Figure 18 GC trace of produced gas from the JP-8 microplasma ball reactor with peaks identified using the MS

The final diagnostic tool that was used was measuring of the soot produced by microplasma ball reactors. After each run with a specific batch of JP-8, the processed fuel was run through filter paper by using a funnel and a vacuum to force the fuel through the paper. After the fuel was run through, the reactor and inside of the chamber was rinsed with isopropyl alcohol in order to get the majority of the soot on the filter paper. The last thing that was done was the reactor itself was submerged in isopropyl alcohol and then put in a sonicator bath to remove the final soot particles from all of the holes and cracks in the nylon reactor. The filter paper was weighed with and without the dried soot particles to get a measurement of the amount of soot that was produced in different modes of the reactor discharging.

3.3.3 Heavy Oil Diagnostics

Similar to the JP-8 reactor diagnostics, Labview was used to monitor the voltage current relationship in order to determine how the reactor was running. The ceramic reactor is less compact and uses bigger balls made of aluminum instead of steel, but the electrical diagnostics still work the same way. The voltage current measurements were plotted as seen in Figure 19 and they were used partially to determine if there was a plasma discharge taking place or if current was just conducting directly through the oil. Because the heavy oil mixtures are much more conductive than JP-8, the relationship appears much more linear. The other important aspect different from the JP-8 voltage current relationship is that for the heavy oil mixtures, the current was time varying adding another layer of complexity.

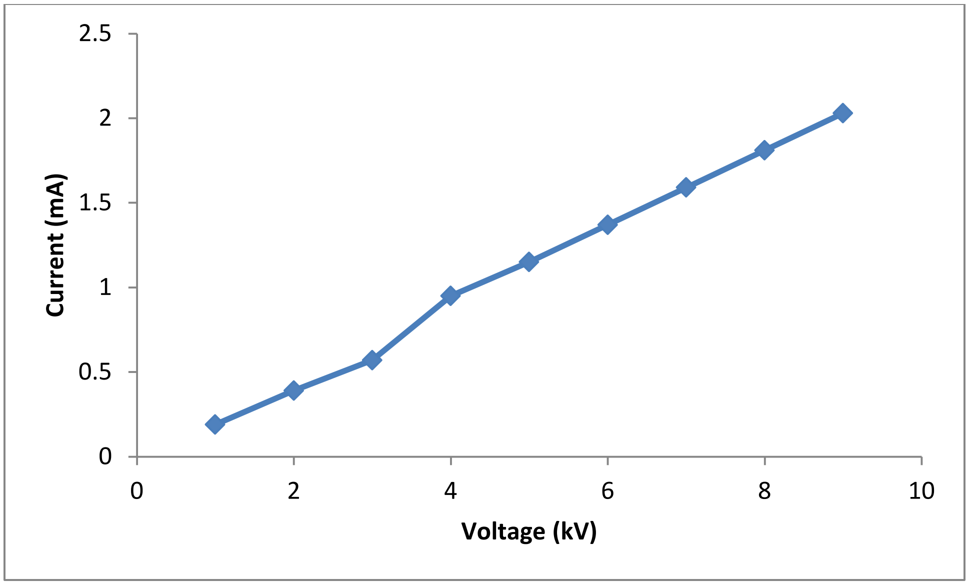


Figure 19 Heavy VR oil mixture voltage current relationship

In addition to using Labview for measuring the voltage current relationship, it was also used to track the voltage and current of the running reactor over time. This is a way to measure the changing conductivity of the heavy oil mixture as it is processed. The process is controlled by limiting the voltage applied in the reactor and letting the current adjust. The voltage and current were periodically measured and plotted as seen in Figure 20. The current and therefore the conductivity of the oil drop off seemingly exponentially. This is used as a gauge to see how much additional processing can take place. Whatever process that reduces the conductivity of the mixture only happens to a certain extent. As a general rule, as the current approaches a stead state value, the oil composition changes less and less until it is no longer being changed.

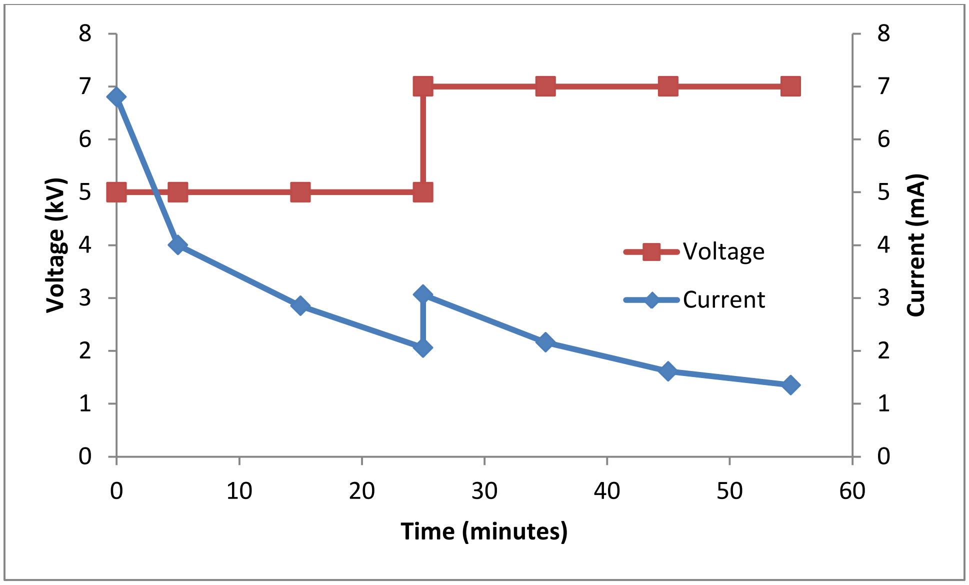


Figure 20 Heavy VR oil mixture voltage and current at different processing times

After processing is complete, the sample needs to be analyzed to determine if the processing made permanent changes to the oil. Since the goal of processing is to decrease the average hydrocarbon chain length, one way to measure that is by viscosity. For longer, more complicated hydrocarbon chain mixtures the viscosity is higher than a mixture with shorter ones. A TA instruments AR-G2 rheometer was used as seen in Figure 21. The viscometer turned a spindle that is in contact with the fluid at a constant rate and measured the torque required to turn the spindle. This allows the shear force and therefore the viscosity to be determined. The base of the viscometer is temperature controlled so that viscosity can be measured as a function of temperature.

Figure 21 Picture of AR-G2 Rheometer used for viscosity measurements of heavy oils [40]

Two types of plots were created using the viscometer, and examples of these can be seen in Figure 22 and Figure 23. The first plot (Figure 22) illustrates how the viscosity changes as the temperature on the rheometer stage ramps up. As expected, the viscosity decreased rather rapidly with increasing temperature. The stage reached a set temperature of a little over 40 degrees Celsius and then it holds at that temperature. The viscosity of the oil continued to drop at this point which can be seen at the tail end of the graphs. This is because the oil has not yet reached a steady state temperature and would continue to increase in temperature. Figure 23 illustrates the change in viscosity as the oil reaches a steady state temperature. Once the rheometer stage reaches the set point of

43C the viscosity is recorded for three minutes creating the viscosity vs. time plot. After this time the temperature is assumed to be steady state and the viscosity constant. In the results discussion for heavy crude oil in chapter 4 the viscosity vs time plot is used to show the viscosity change due to processing by comparing the viscosity at the end of the three minute period. It is in that chapter that the plot will be explained further.

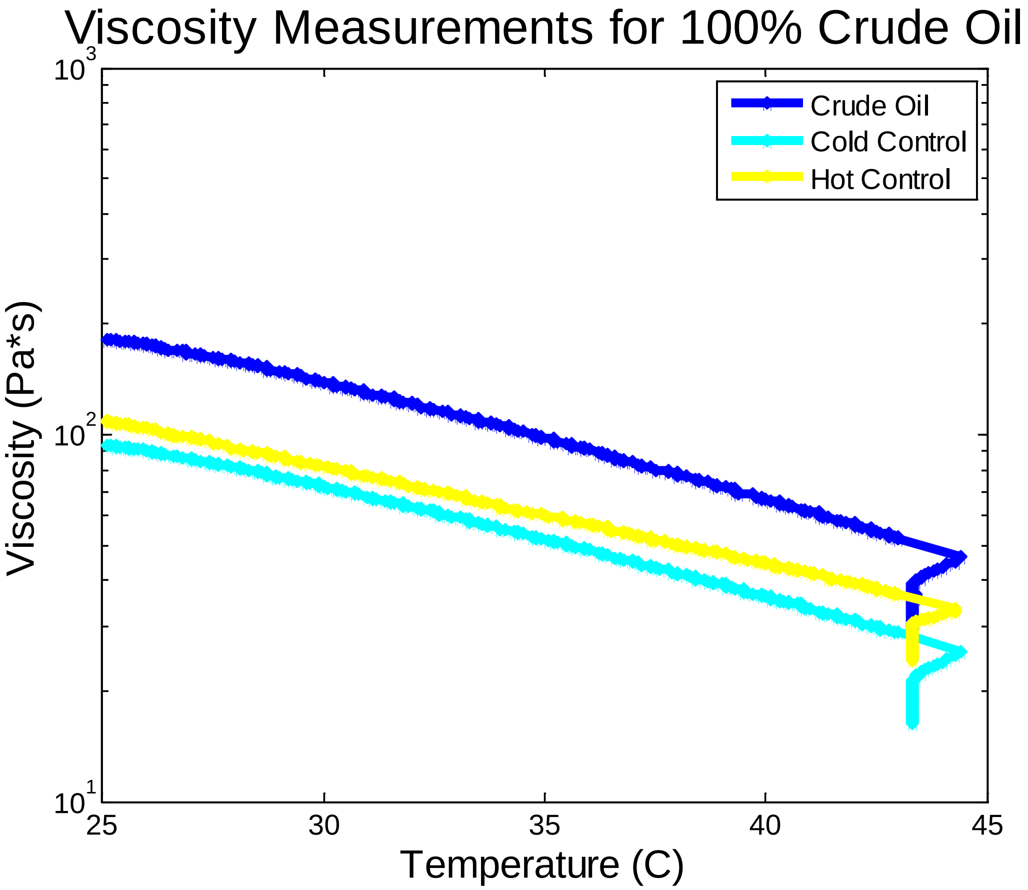


Figure 22 Viscosity as a function of rheometer platform temperature for heavy crude oil

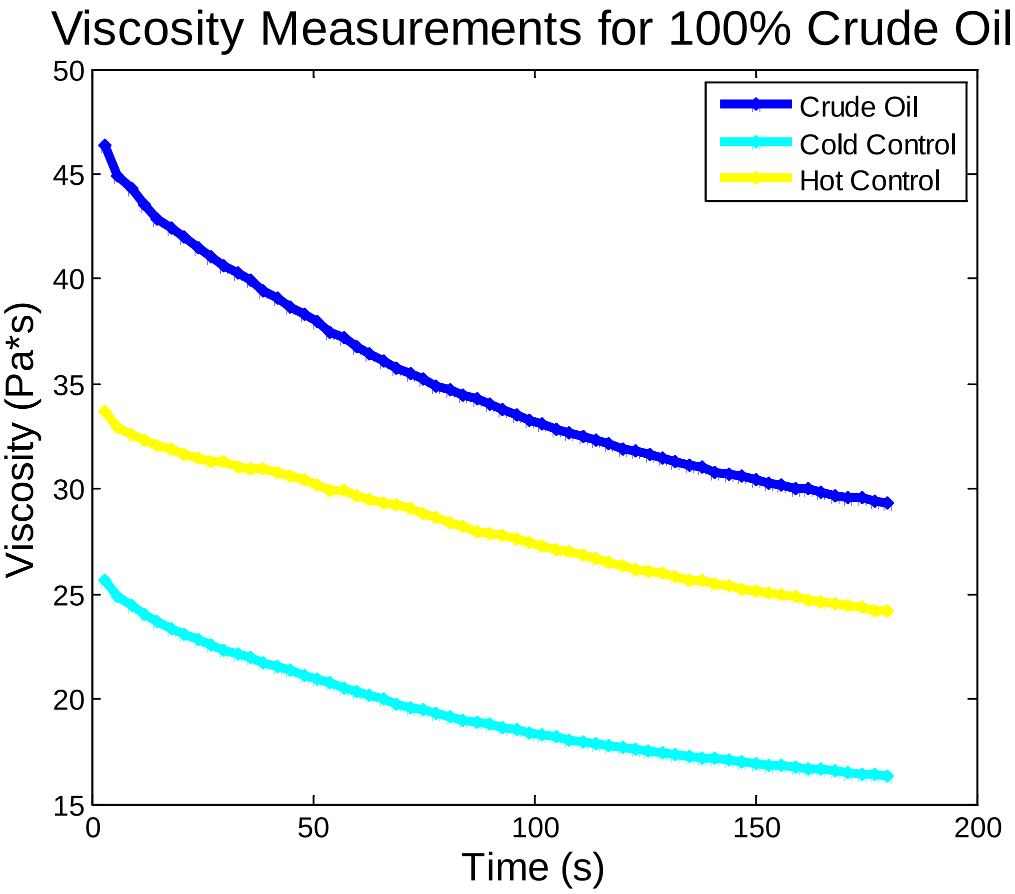


Figure 23 Viscosity as a function of time for the rheometer platform temperature being held at 43 C

3.4 Procedures

3.4.1 JP-8 Experimental Setup Procedures

A couple of different experiments were run using JP-8; the general experimental procedure is as follows. First, the nylon reactor was placed in the container and JP-8 was poured over it until it was completely submerged. The electrodes on the reactor were hooked up through the lid so they could be attached to wires on the exterior of the chamber. The lid was then sealed using nylon screws and a silicon gasket. A 35 ml syringe with a ball valve was screwed onto the top of the chamber in order to capture any produced gas as shown in Figure 9. The syringe was pulled out to test if the chamber was sealed properly or not. Once the reactor was hooked into the circuit with the high voltage power supply, the voltage is slowly ramped up to the desired voltage and the current is allowed to adjust as appropriate. The process is timed until the syringe is filled with 35 ml of gas. Based on which voltage the reactor runs at this time will change. Total energy input remains constant however even with discharge power changing.

After the processing was completed and the syringe was filled, the gas was taken and injected into the GC MS setup from the syringe. The calibrated GC gives the relative concentrations of gas components by different area peaks. The MS identifies the specific compound the peaks represent. Unless the same JP-8 is going to be used in the next experiment, it is removed and run through a filter to capture the soot that was produced. The reactor is also run through a sonicator to clean off the remainder of the soot. All of the soot is then weighed. If the JP-8 is going to be run again for a higher total energy input to processing the reactor lid is never opened and no liquid or solid is removed, only the gas is removed and run through the GC MS setup.

3.4.2 Heavy Oil Mixing

In order for the heavy oil to have a low enough viscosity so that it can be processed it needs to be mixed with a less viscous fluid. While the viscosity can be decrease by raising the temperature high enough, it is easier and more efficient to do a combination of things to lower the viscosity. The lower viscosity oil also serves as a hydrogen donor to the heavy oil.

There are two methods for mixing heavy oil that were used to go along with the two types of heavy oil. The first type of heavy oil is crude oil. As mentioned previously it has a whole wide range of hydrocarbons mixed in. The second type of heavy oil is the vacuum residuals from the bottom of distillation towers. This heavy oil is even more viscous than the crude and is almost exclusively long chain hydrocarbons. The two primary light oils that these heavy oils were mixed with was mineral oil and refinery cycle oil. Mineral oil is just a standard oil often used as a lubricant, and cycle oil is a refinery cocktail that is used to move different oils around in the refinery.

In order to mix the heavy crude oil with mineral or cycle oil it first has to be heated so that it could pour out of the can. This was just done in an old oven where the oil can was left in at a little over 100 Celsius for a couple of minutes. The mixtures were made by pouring in both components on a percent volume basis. The heavy crude oil mixture was then stirred until it was completely mixed. For the vacuum residual, the mixing was done differently. Since it was so much more viscous it had to be heated up considerably hotter. Instead of mixing the vacuum residual directly with the cycle oil, the vacuum residual was frozen using liquid nitrogen and then crushed into a fine powder. The mixture was made on a per mass basis. The vacuum residual was weighed out and the appropriate amount of cycle oil was mixed in with it. The mixture was then heated and stirred over a couple of days in order to completely mix the two parts without any chunks in the mixture.

3.4.3 Heavy Oil Experiments

Most of the heavy oil processing experiments were done inside the pressure vessel. A diagram breaking down the step by step processes for the pressure vessel experiments is given in After the oil to be processed was completely mixed it was poured into a glass bowl containing the ceramic microplasma ball reactor until the reactor was completely covered. If the experiment was being run inside of the pressure vessel, a small glass jar was filled to act as a control inside of the vessel where it was exposed to heat and pressure. Another small glass jar was filled with oil and kept as a room temperature control sample.

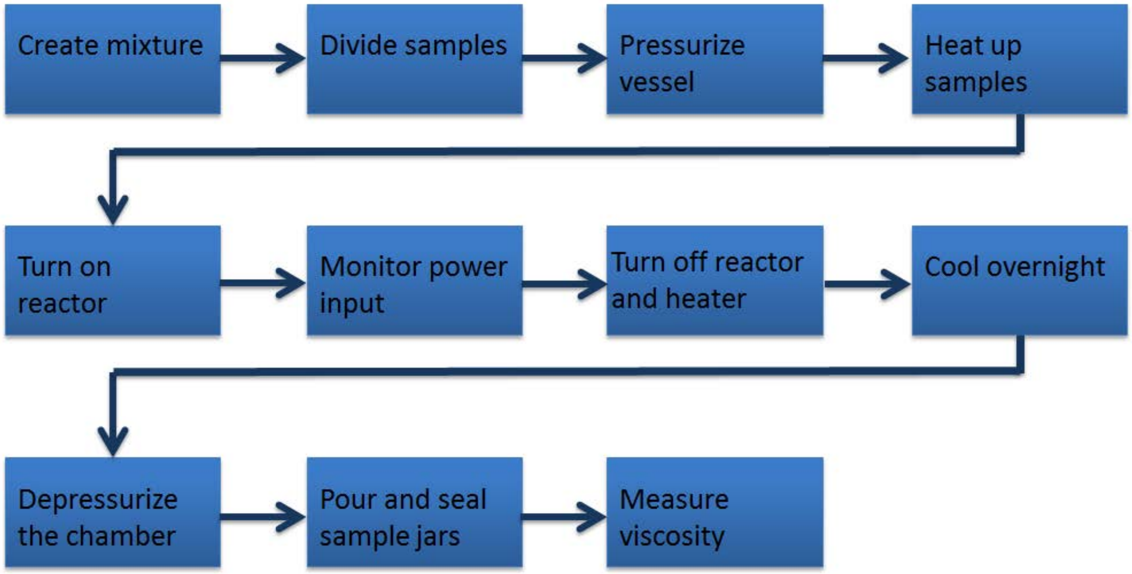


Figure 24 Diagram outlining the heavy oil pressure vessel processing experiment procedure

The reactor was then hooked up to external electrical feed throughs in the pressure vessel. A thermocouple was placed in the control sample that was left in the vessel in order to accurately monitor temperature. The pressure vessel door was shut and sealed. Using a compressed Nitrogen gas cylinder the vessel was brought to close to the desired pressure. The heating control unit was then plugged in and the chamber heated to the set point temperature. Once the correct steady state temperature was reached the pressure was adjusted in order to get the desired processing temperature.

The high voltage power supply is then turned on and set for the desired voltage and current settings. The oil is processed until a given amount of energy is put in. This is measured by integrating the power measurements taken by Labview. After the processing is completed, the vessel is allowed to cool while still at high pressure in hopes to prevent as many hydrocarbons from escaping. The vessel is left overnight to cool, and in the morning the pressure is released and the chamber opened. The samples are taken out and a lid is screwed on. The processed oil is poured into another jar that can be sealed for later measurements.

The sealed jars were left to sit anywhere from a couple days to a couple weeks before they were taken to be measured because the lab with the viscometer was in a separate location. The temperature of the base was ramped up to 40 degrees Celsius and held there for 120 seconds so that the oil has time to reach an equilibrium temperature. The viscosity for the last 120 seconds was recorded and plotted.

4. RESULTS AND DISCUSSION

4.1 Optimization of the Ball Reactor

The objective of this set of experiments was to understand how the ball reactor works so that it could be optimized as well as use the reactor to crack JP-8 and efficiently make Liquefied Petroleum Gas (LPG) consisting mostly of C_3 hydrocarbons.

4.1.1 Ball and Column Size

The motivation for the JP-8 to propane conversion comes from a request for information (RFI) from the Defense Advanced Research Projects Agency (DARPA) and the general requirements for the JP-8 conversion devise are outlined in Table 2 [41]. While it is known that using a microplasma generated from a bouncing ball this conversion can take place, it is important to optimize this process in order to meet the different efficiency requirements outlined below. The first thing that was optimized was the ball and column sizing.

Table 2 Goals for microplasma reactor [41]

	Threshold	Goal
Total System Size	<2 cubic meters	<.2 cubic meters
Maximum Single Dimension	< 2 meters	<.5 meters
Output Rate of LPG	>.2 kg/hour	>10 kg/hour
Fuel Conversion Efficiency	> 5%	>30%
Startup Time	< 30 minutes	<5 minutes

In order to produce the maximum amount of product, the total reactor power is desired to be maximized. However the specific energy input of a single discharge must remain small in order to keep from completely obliterating the hydrocarbon. This is measured by the amount of charge passing through each ball and column. The charge on each ball can be calculated using a dielectric constant of mineral oil of 2.3 and a field enhancement factor of $\beta = 4$. The frequency with which the discharges happen can be measured. Both of these can be combined to get current. The other factor that is important is space efficiency. Since a smaller size reactor was considered more efficient, the parameter chosen to maximize was the current density. It was defined as the current transported through an individual ball and column divided by the volume of the column. The formulas used to calculate ball charge and current density can be seen in the equations below.

$$q = \beta k \varepsilon_0 d^2 E_0 \tag{1}$$

$$J = \frac{qf}{V} \tag{2}$$

A whole range of different types of balls were tested using a single column setup with an adjustable electrode gap as seen in Figure 25. The sizes ranged from 1/4 inch balls to 1/32 inch balls of both aluminum and steel. For each case the current density was determined at a non-dimensional column height of length over diameter, and at a voltage between the lift off voltage and the breakdown voltage. The lift off voltage is the voltage at which the ball begins to move, and the breakdown voltage is the voltage at which a spark discharge happens through the whole column and through the ball as illustrated in Figure 26. This type of discharge is high energy and thermal and is therefore undesirable because it contributes to soot formation. An example of this is plotted in Figure 27. The setup that allowed for the highest current density was the 1/32 inch aluminum ball. As seen on the plot, the L/D ratio where the maximum current density was attained was between 1.5 and 2. The problem with a ball this small is that it is almost impossible to machine columns of this size while allowing for fluid to easily flow through the column. For this reason a larger size ball was used in the prototype of the microplasma ball reactor.

Figure 25 Adjustable electrode setup for ball optimization study

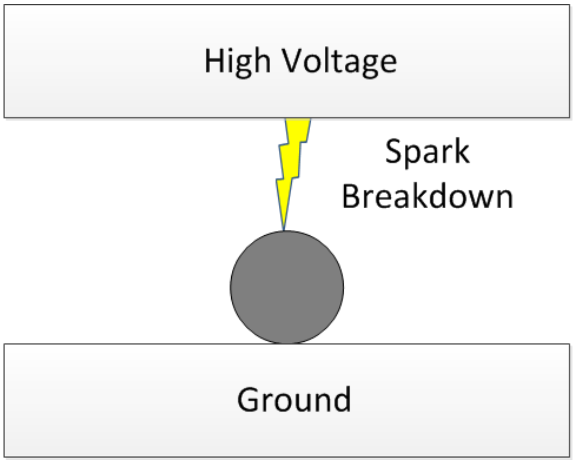


Figure 26 Diagram of a spark discharge that occurs when the applied voltage is enough to overcome the dielectric strengths of the liquid medium

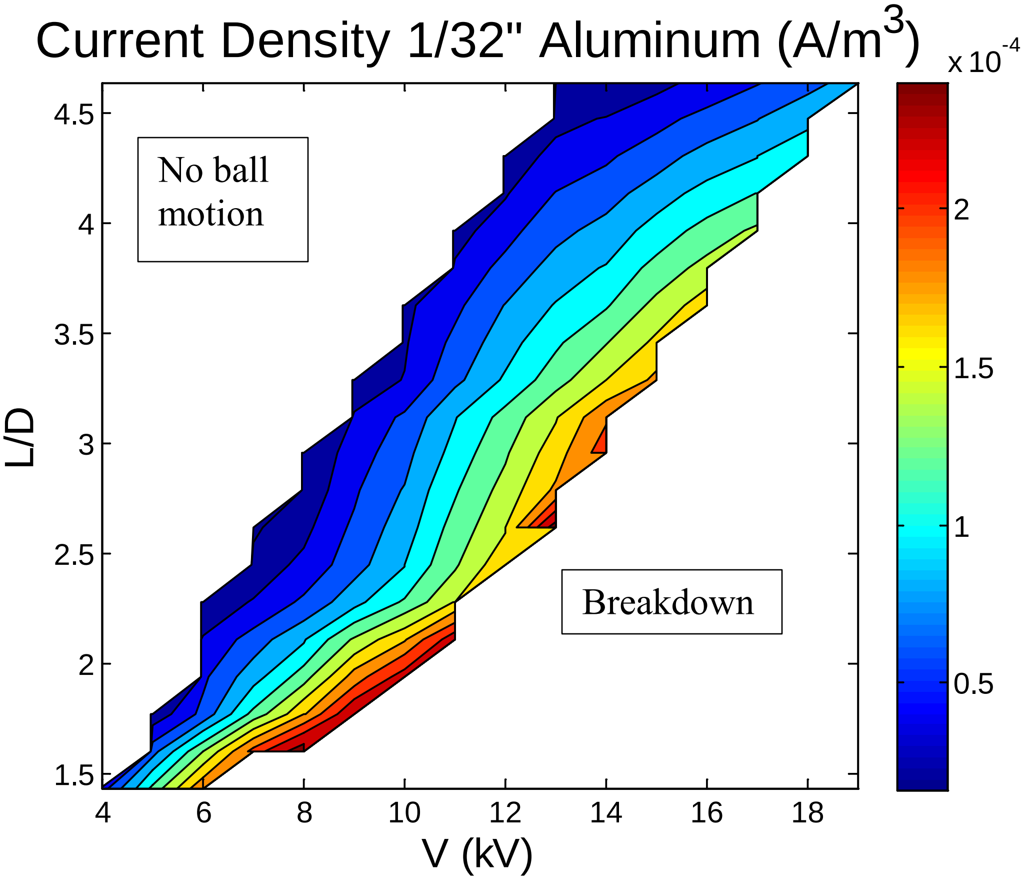


Figure 27 Current density plot for 1/32'' aluminum ball as a function of the L/D ratio and the applied discharge voltage

Instead of making the reactor with 1/32 inch balls, 1/8 inch balls were used. These are larger making them easier to handle and the columns of the reactor easier to machine. While smaller balls move faster through the fluid and have a higher frequency, they carry less charge so many more of them are needed to maintain a high power input. The other advantage of the 1/8 inch steel ball is the fact that it is relatively inexpensive along with the fact that it is magnetic making the balls easy to extract from the reactor and clean. Since hundreds of thousands of these balls will be needed to make a full scale reactor price per ball is important to consider. As previously mentioned, the frequency was what was actually measured, and from this the current density was calculated. The plots of the measured frequency and calculated current density can be seen in Figure 28 and Figure 29 respectively. It can be seen that the highest bounce frequency does not equate to the highest current density. Once again, the optimum current density occurs at a L/D ratio of about 2 because the operating voltage also plays into the current density. This ratio was used to design the prototype nylon ball reactor.

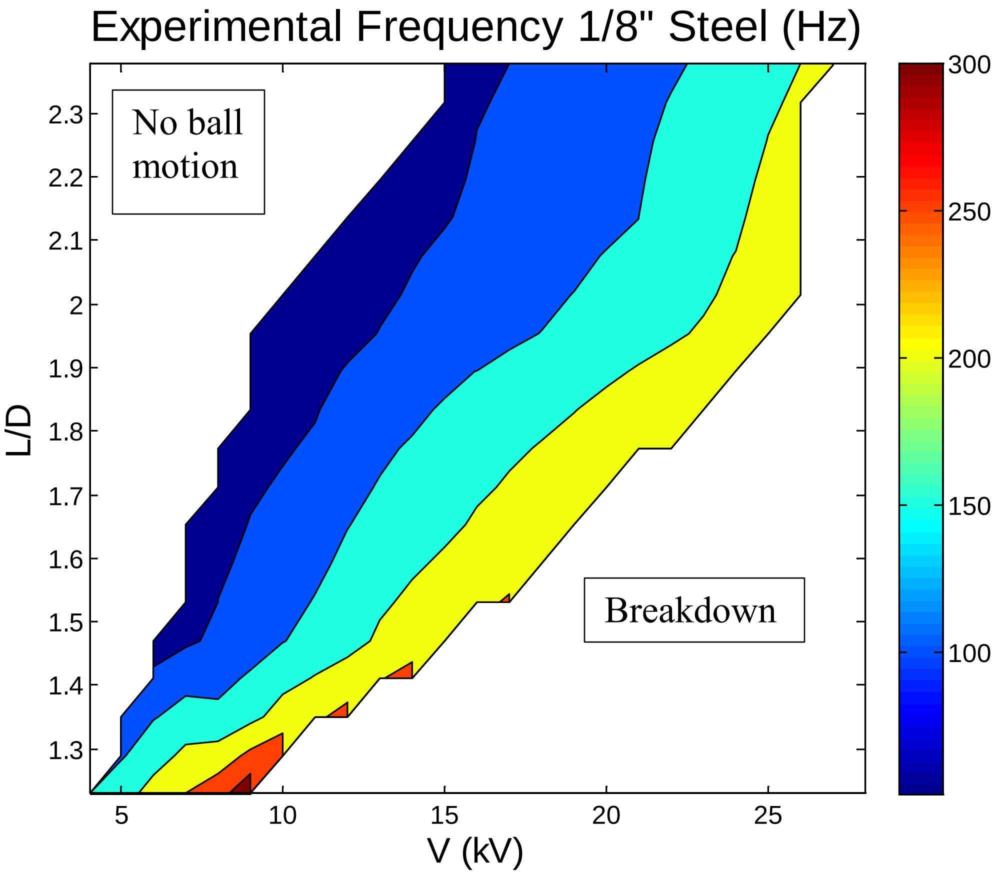


Figure 28 Measured frequency of 1/8'' steel ball bouncing in single column as a function of the L/D ratio and the applied discharge voltage

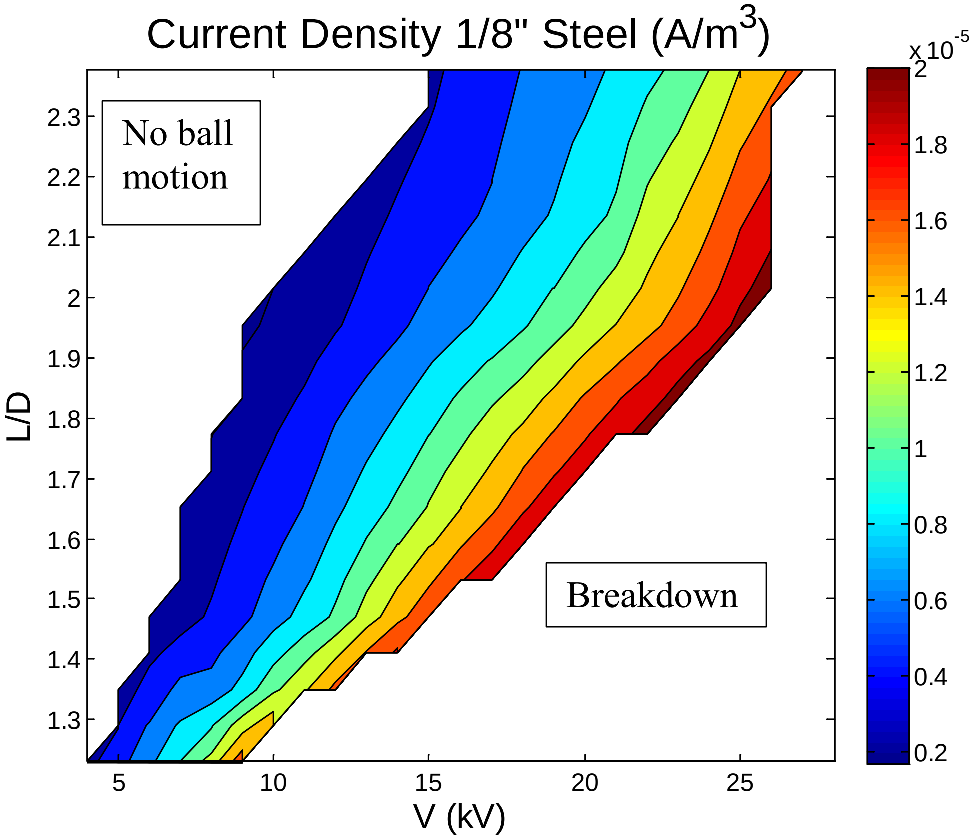


Figure 29 Calculated current density for 1/8'' steel ball in single column as a function of L/D ratio and the applied discharge voltage which is the setup used in the final design of the nylon ball reactor

When designing the nylon prototype microplasma ball reactor other observations beside the optimum L/D ratio were taken into account. Since the gas produced by the single bouncing ball was getting trapped, the columns were made to be open on top and bottom allowing air to escape and fluid to flow through easily. Holes on the side were drilled in order to hold wire electrodes in place securely and also allow for fluid and gas flow.

4.1.2 Ball Density

Another secondary parameter to optimize in the reactor was the density of the ball. Since a heavy ball requires more force to overcome gravity or a light ball needs more force to overcome buoyancy. It is thought that while the ball will travel slower working against gravity or buoyancy, it will travel faster when the electric field is working with these forces. Table 3 below summarized the results with varying ball density in mineral oil with the same ball size. The neutral density ball had the highest bounce frequency. The reason for this is the viscous friction creates more losses with balls with a density much different than that of the fluid they are in.

Table 3 Table of 1/4" ball bounce frequency compared with density relative to mineral oil

Density (Kg/m^3)	Relative Density (Kg/m^3)	Frequency (Hz)	Ball Material
750	-100	29	hollow aluminum
901	51	32.5	neutral density
8200	7350	20	steel
2700	1850	29.5	solid aluminum
850	0	0	mineral oil

As mentioned previously, steel was the material chosen for the balls in the prototype microplasma ball reactor. Neutral density balls are extremely expensive to make. Even aluminum balls are relatively expensive. While the reactor would work more efficiently with either of these, steel was chosen for its cheapness and ease of use.

4.2 JP-8 Conversion

4.2.1 Flow Rate of Gas Product

When determining the efficiency of the JP-8 conversion two things must be taken into account. The percentage of the product that is the desired product and the amount of total product made. First experiments were done to measure the total amount of product being produced. Using the rapid prototyped nylon 300 column microplasma ball reactor in the sealed container, the flow rate of gas produced from running the reactor in JP-8. The power was varied and the flow rate measured with a stopwatch and syringe. The results are seen in Figure 30. The relationship is linear and is represented by the equation on the graph. This equation was used in later calculations. The power can be varied not only by increasing the voltage, but also by adding other columns in parallel.

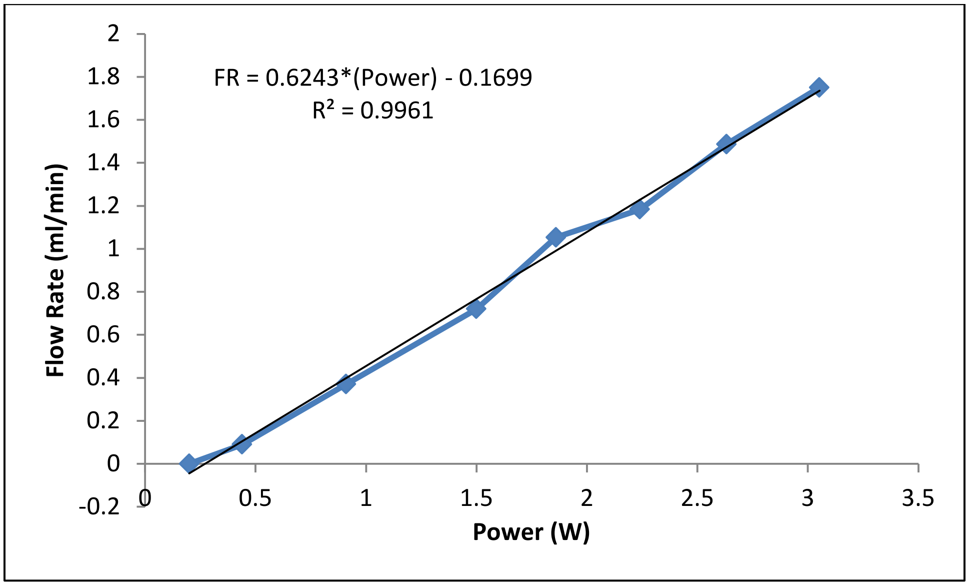


Figure 30 Flow rate of gas produced by JP-8 processing at different reactor powers

In order to verify that the reactor can be scaled up by adding additional columns in parallel an experiment was done comparing 100 working columns at a certain voltage with 300 working columns at a certain voltage to verify that the former ran at 1/3 the current and therefore 1/3 the power consumption. In Figure 31 the voltage current relationship for 100, 200 and 300 working columns was given along with the scaled up predicted VI from the 100 column data. The scaled up predictions are fairly accurate to the measured values illustrating that each ball and column is its own separate entity and the reactor can be scaled up linearly by adding additional columns.

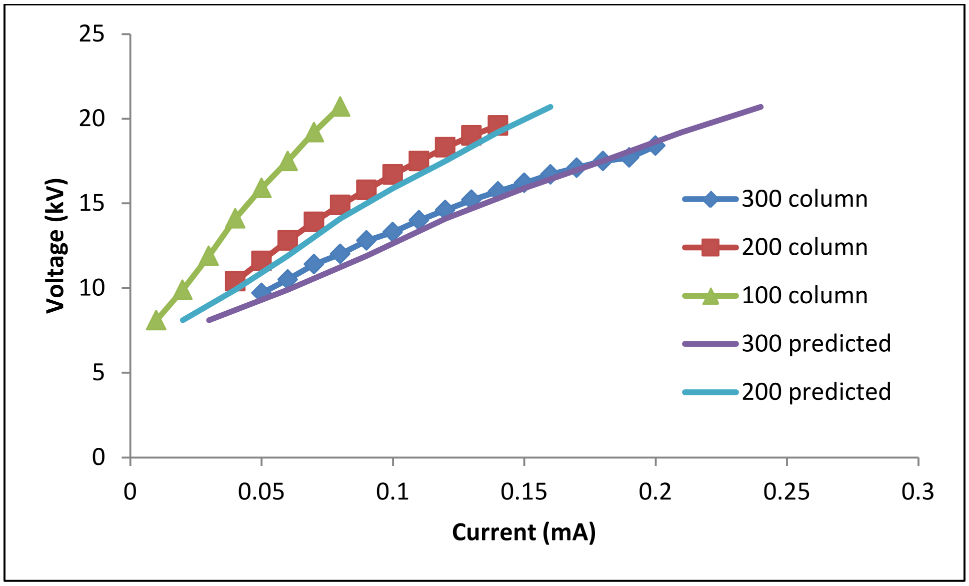


Figure 31 Plot to verify the linear scaling up of the microplasma ball reactor

In addition to reactor power being scaled up linearly using the method of adding more columns, flow rate also scales up regardless of the operating voltage. The reactor was run at the highest available voltage for 100 columns producing 1/3 of the power.

Flow rate of gas produced in this case matches Figure 30 exactly with the 300 column reactor running at a lower voltage to produce 1/3 the maximum power. Reactor power is the only important parameter in determining the flow rate of gas produced from the microplasma ball reactor in JP-8.

4.2.2 Composition of Gas Product

The other aspect of the reactor efficiency is the percentage of produced gas that is the desired product. Not only was the flow rate measured, but the composition of the gas that was produced was determined by using a GC and MS setup in series. By just running the produced gas through the MS a mass spectrum, seen in Figure 32, was developed that shows the peaks for the different hydrocarbons in the gas. The gas mostly consists of Hydrogen through C_3 hydrocarbons with a few C_4 and higher hydrocarbons mixed in. Only hydrocarbons through C_3 were detectable with the HID on the GC and those are the only hydrocarbons considered moving forward.

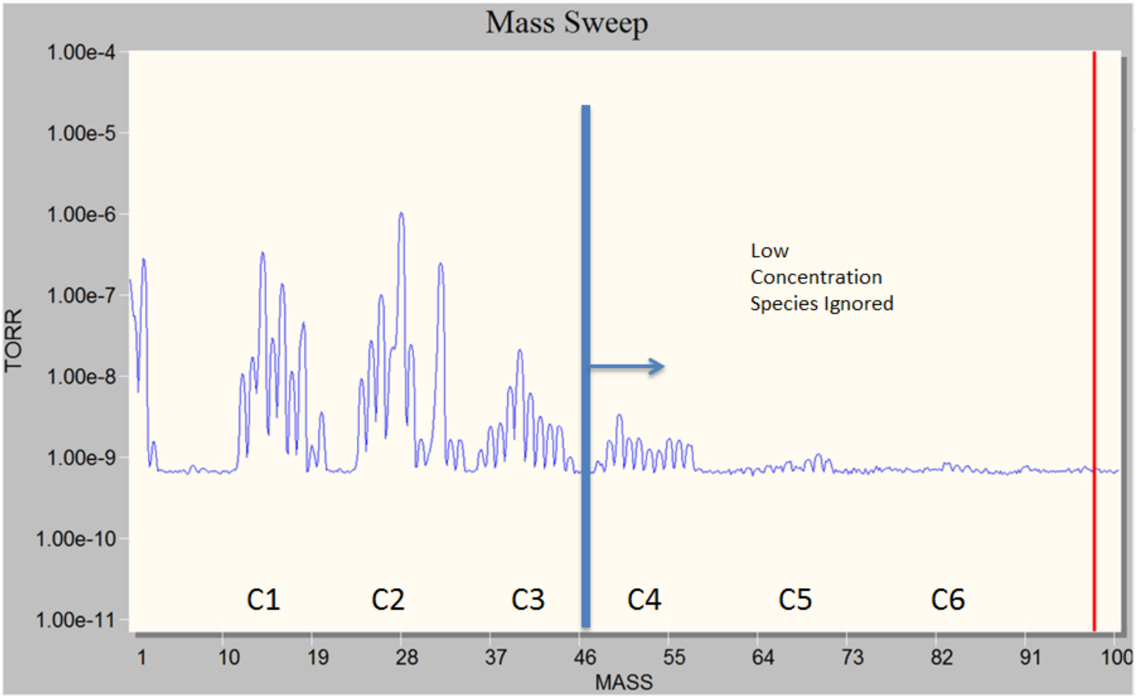


Figure 32 Mass spectrum of gas produced from microplasma ball reactor in JP-8

After the flow rate was measured by filling up the syringe, the captured gas was then put through the GC which had peaks identified by the MS. The HID had been calibrated previously by a hydrocarbon cocktail gas of known concentrations. The reactor was run at three different powers represented by three reactor voltages. The lowest voltage 10kV represents the lowest voltage where the balls still move. This also represents the lowest specific energy input. 17kV represents the highest voltage where breakdowns through the column do not happen. 19kV is the voltage where sporadic breakdowns in the columns are occurring. The mass percentages of the various components are shown below in Figure 33. Mostly hydrogen, methane, and ethylene are produced. The desired C_3 hydrocarbons make up just over 5% of the total mass. The other important observation is that the reactor voltage and therefore the discharge energy had no effect on the composition of gas produced over the range tested.

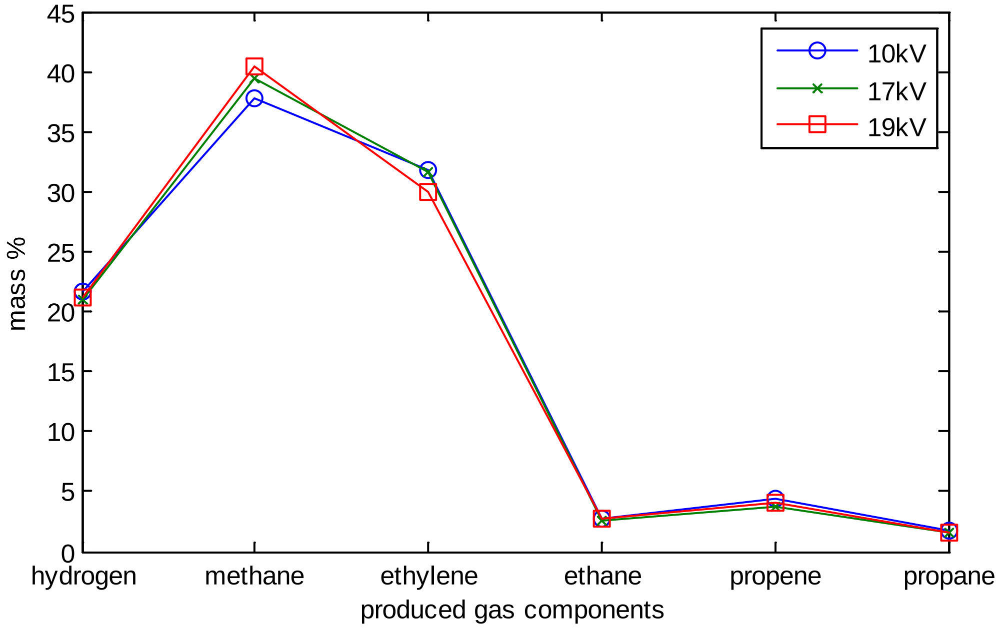


Figure 33 Components of the produced gas for different discharge energies

The next experiment that was done tested how the composition of the produced gas changed in regard to the total amount of energy put into processing a specific batch of JP-8. During the time it takes for the reactor to process one syringe full of gas, 35kJ of energy was used by the reactor. The reactor was run at 17kV so it took about 30 minutes of run time to fill an entire syringe. The results can be seen in Figure 34. As the total energy input increased, the composition of the gaseous product changed. Production shifted away from hydrogen and methane an instead higher hydrocarbons were created. In the higher energy cases around 14% of the product by mass is the desired C_3

component, which is almost three times as efficient as C_3 production initially. Figure 35 illustrates the same results in a different format. While there is an error of somewhere on the order of 3% with a GC, it is evident that as the total energy increases the gaseous product concentration of hydrogen and methane decrease while C_2 and C_3 hydrocarbons increase in concentration.

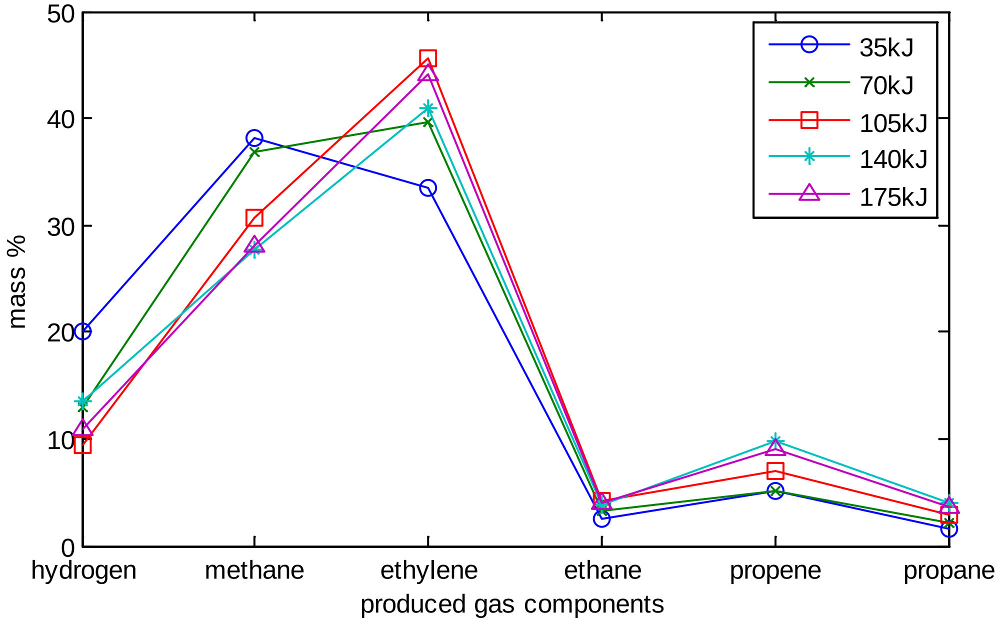


Figure 34 Components of the produced gas for different total input energies

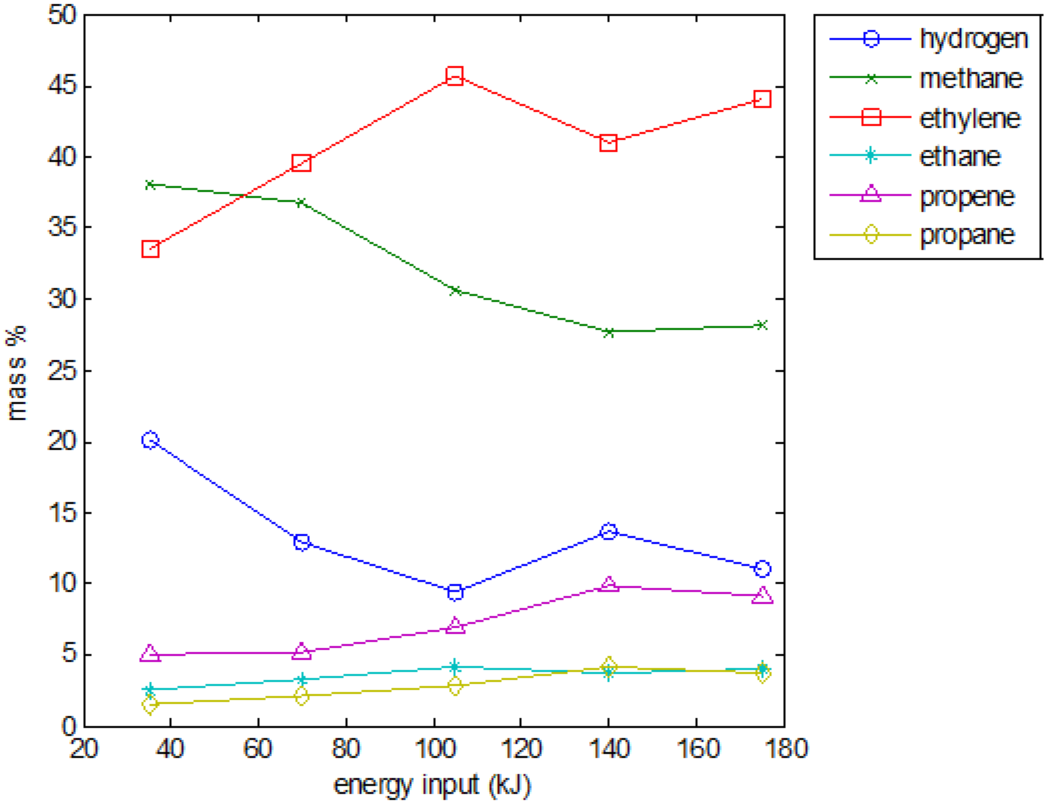


Figure 35 Change in gas component percentage for different input energies

It is evident that at higher total energy input there is some sort of shift in the reactions that are taking place to break up and recombine the hydrocarbons. Another interesting observation is that the gas production rate remains constant even though the composition is changing. The exact chemical reactions taking place in this case are unknown. As the energy input continues to increase, soot production increases making the JP-8 quite dirty.

4.2.3 Soot Production

As these hydrocarbon cracking reactions induced by the plasma are taking place the products are not just gaseous. There is a solid carbon product created generally referred to as soot. The production of soot was monitored and whenever used JP-8 was removed soot was filtered out and weighed to determine how much was produced. A picture of the filter papers with soot with different weights produced for different voltage runs is seen below in Figure 36.

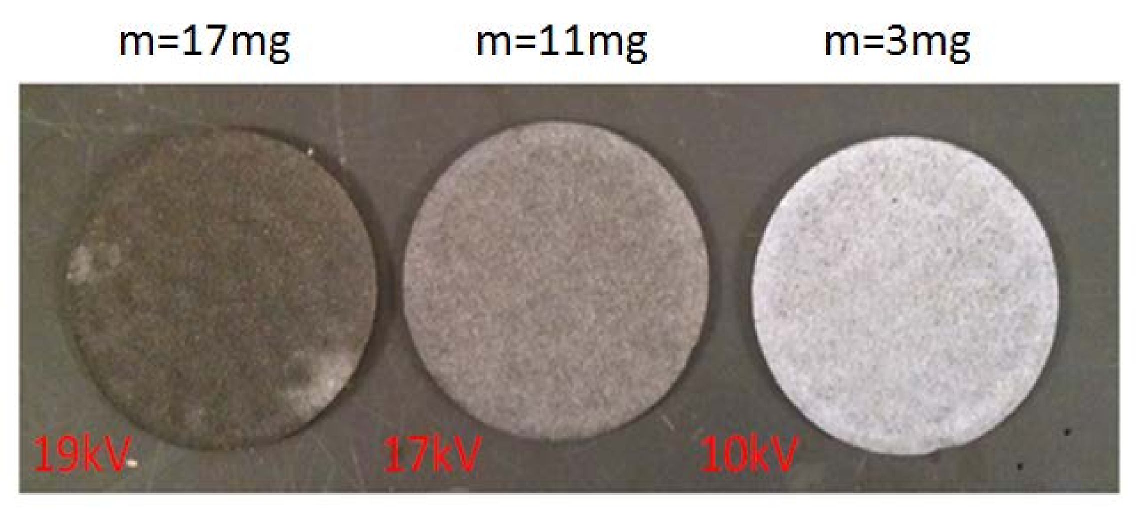


Figure 36 Soot production from microplasma ball reactor in JP-8 for same total input energy of 35kJ and various discharge voltages

Even though the composition of produced gas is the same for these three cases, there is clearly different chemistry taking place. The lower specific input energy has lower energy discharges which produce less soot. It is unclear exactly what role soot plays in reactions as time goes on. Because the balls are constantly moving there is little risk of the soot clogging up the reactor.

4.2.4 Scaling Up the Reactor

With the knowledge gained from all the experiments, estimates were done to see what a reactor big enough to produce a usable amount of fuel would look like. From the experiments with the small scaled reactor, the necessary power for a specific flow rate could be determined using the formula in Figure 30. By assuming operation at the maximum voltage before breakdown and that each ball and column unit operated independently and identically the power per column could be determined and then the total number of columns to reach the threshold flow rate seen in Table 4.

Table 4 Comparison of the goal and actual specifications for the microplasma ball reactor

	Threshold	Goal	Small Scale Reactor	Scaled up Reactor
Total System Size	<2 cubic meters	<.2 cubic meters	6.6e-5 cubic meters	1.7 cubic meters
Maximum Single Dimension	< 2 meters	<.5 meters	.05 meters	1.2 meters
Output Rate of LPG	>.2 kg/hour	>10 kg/hour	1.4e-5 kg/hour	.2 kg/hour
Fuel Conversion Efficiency	> 5%	>30%	13%	13%
Startup Time	< 30 minutes	<5 minutes	none	none
Number of Columns			300	10.5 million

The output flow rate was determined by calculating the mass flow rate from the volume flow rate. The gas density was estimated to be 1.13 kg/m^3 by multiplying the component density by the mole fraction of the component. Then it was assumed that 13% of the produced gas was the desired LPG product thus providing a mass flow rate for LPG.

The size of the scaled up reactor was determined by assuming the balls could be packed in a honeycomb fashion leading to the packing density being increased by a factor of 1/3. By making the reactor square the dimensions were set as well. The reactor could be optimized by a parameter different than output rate to produce slightly different results. The important thing is that this technology has the ability to produce results right now. The ball and fluid motion along with the reaction chemistry could be studied more in depth to increase the efficiency of this process making it even more economical.

4.3 Heavy Oil Conversion

The objective of this set of experiments was to use the ball reactor technology that was developed in the JP-8 experiments to crack heavy oils. The goal is to decrease the C/H ratio and shorten the average hydrocarbon chain length effectively permanently reducing the viscosity.

4.3.1 Electrical Conductivity Experiments

As mentioned previously, in order to process the heavy oil two things had to be done to reduce the viscosity of the oil enough so that the balls in the reactor could move. The heavy oil was heated up during processing, and it was mixed with lighter oils. Mixing with lighter oils also had the added effect of a hydrogen donor present in the oil whenever the cracking was taking place. Both of these techniques to reduce initial viscosity of the oil for the purposes of operating the microplasma ball reactor also have the added effect of increasing the conductivity.

A high oil conductivity is detrimental to the reactor efficiency. When the oil mixture is conductive current does not only travel through the microplasma discharges between the ball and electrode but it also travels directly through the oil. This contributes to heating the oil making the problem even worse, and is an electrical inefficiency. In order to find an optimum oil mixture the conductivity was measured for different temperatures and compositions.

The setup used was almost exactly the same as the circuit described in the previous section. The only difference was instead of having a reactor hooked up in the circuit, two parallel plate electrodes were hooked up and submerged in the oil mixture. The plates are both one square inch and were set apart from each other a specific distance that was kept constant throughout all the conductivity tests. The current that was measured is only the current traveling from one plate to the other through the oil mixture. The current was measured at varying voltage and the slope of the current voltage line was calculated to be the conductivity. The results are seen below in Figure 37.

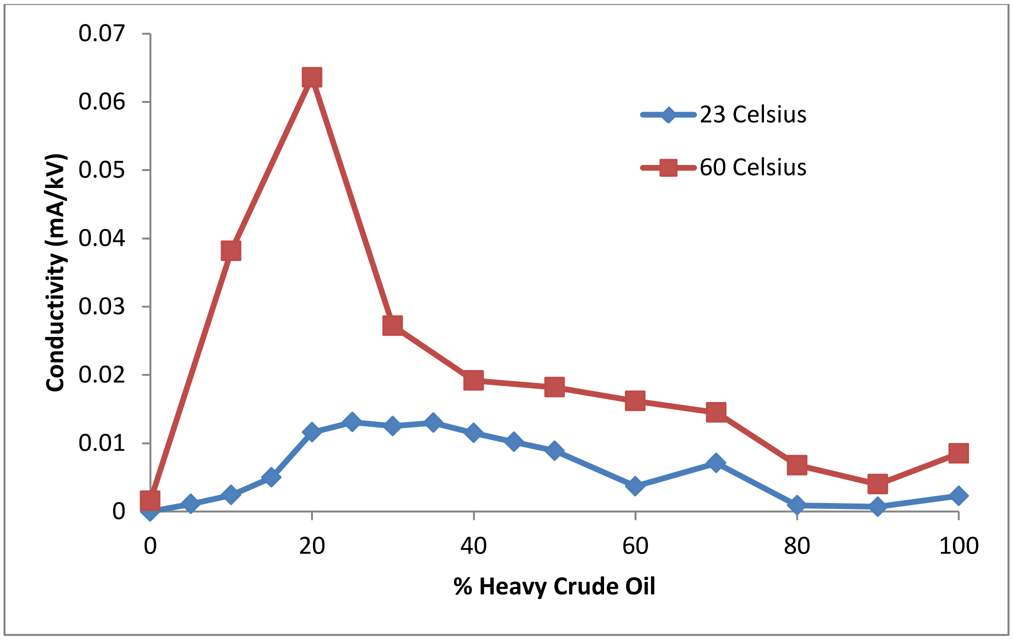


Figure 37 Conductivity of heavy crude oil at various compositions and temperatures

In these experiments the remaining percent that is not heavy crude oil is mineral oil which was also used in our microplasma ball reactor experiments as a hydrogen donor. In general higher temperatures produce higher conductivities, and there is a specific concentration that produces the highest conductivity at a specific temperature and it is usually around 20-30% heavy oil. In our processing experiments it is desirable to process more heavy oil than mineral oil, so generally around 70-80% heavy oil mixtures were used. This is on the lower end of conductivity for a specific temperature, but there is enough mineral oil to reduce the viscosity enough to process the oil mixture.

4.3.2 Nylon Ball Reactor

Initially a nylon microplasma ball reactor for processing heavy oil was created similar to the one used to process JP-8 in Figure 7. This new reactor seen in Figure 38 had the same overall dimensions so that it could fit into the nylon container in Figure 9. In this way the processing of the heavy oil mixtures had almost the exact same setup as the JP-8 processing. The only differences were 1/4 inch hollow aluminum balls were used instead of 1/8 inch steel balls, and the setup was heated to run at a higher temperature. Both of these things were done to decrease the effect of viscous forces on the motion of the balls.

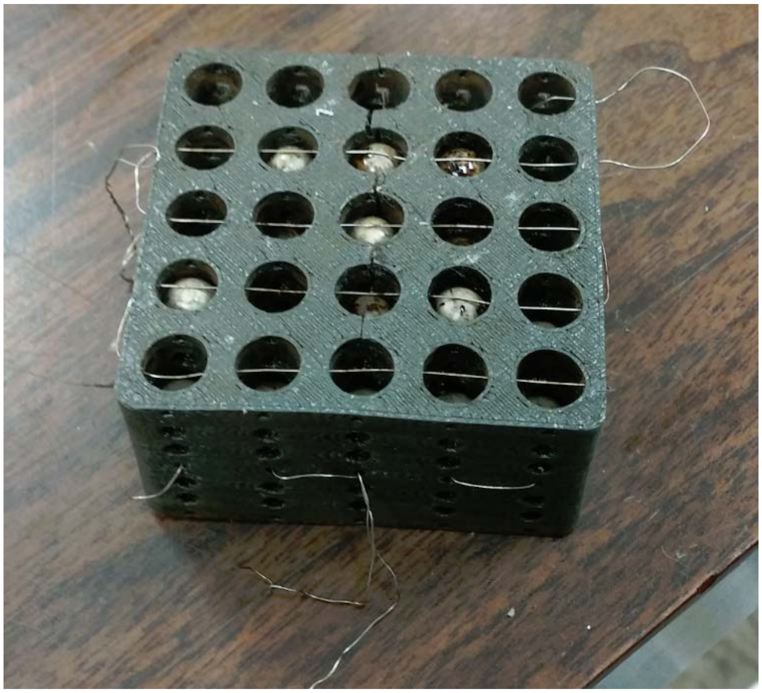


Figure 38 Used 1/4 inch nylon microplasma ball reactor that is cracked and warped from the heat in processing

The results from these experiments were inconsistent. Sometimes there would be considerable viscosity reduction and sometimes not. Even repeating conditions to get similar results were difficult to do. The heating methods for these experiments were open loop making it difficult to control the temperature accurately. The conductivity of the oil mixture was so sensitive to temperature the ball reactor would go from working to not working in a matter of a few degrees. Since the mixture was black it was sometimes difficult to tell if the balls were actually moving and a plasma discharge was taking place. As seen in Figure 38 the heat stress caused the reactor to crack and start to come apart. There was also a concern that light hydrocarbons that were being created were evaporating off.

From these experiments it was learned that it is possible to reduce viscosity permanently, and a better control mechanism was needed to control the operating parameters especially temperature. A high pressure environment was desirable in order to prevent light hydrocarbons from boiling off. In addition a reactor that resistant to heat and pressure is needed. It was decided to make the reactor out of machinable alumina silicate ceramic and run experiments inside of a pressure vessel with controlled temperature and pressure.

4.3.3 Temperature and Pressure Viscosity Change

In order to understand exactly how pressure and temperature affect viscosity a set of control experiments were done. All samples were left untreated by the plasma reactor. The viscosity was measured after a sample of 80% crude oil and 20% Cycle oil was exposed to open air, 130F at atmospheric pressure, 250 psi at room temperature with one sample closed immediately after so no gas could escape and one sample left open. The results can be seen and explained in Figure 39 and Table 5.

Table 5 Description of the legend entries for Figure 39

Legend	Description
130 F	The oil mixture was held at 130 degrees for the length of a processing run at atmospheric pressure
250 psi closed	The oil mixture was held at 250 psig in the vessel for the length of a processing run at room temperature and was sealed immediately after processing
250 psi open	The oil mixture was held at 250 psig in the vessel for the length of a processing run at room temperature and was left open after processing
Temp Control	The control mixture for the temperature run left outside the vessel at atmospheric conditions
Pressure Control	The control mixture for the pressure run left outside the vessel at atmospheric conditions

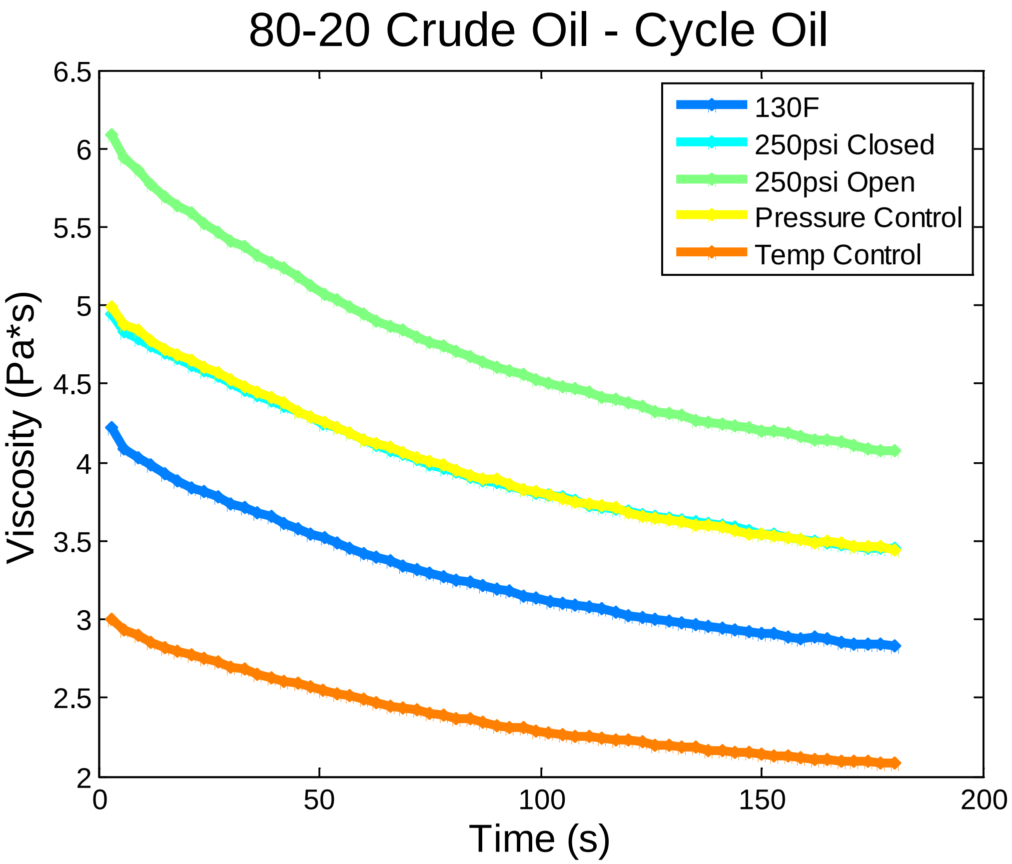


Figure 39 Viscosity measurements for oil mixtures exposed to temperature and pressure with the legend description in Table 5

It can be seen that independently both temperature and pressure increase the viscosity of a mixture of oil. Temperature is the most intuitive because high temperature will boil off light hydrocarbons leaving the heavier and more viscous hydrocarbon chains behind. For pressure, it is clear that a higher dissolved gas content reduces viscosity as seen by the fact that the sample where dissolved nitrogen was allowed to escape had a higher viscosity. However it is possible that pressure deformed some of the hydrocarbon molecules making the viscosity higher as well. Another possible explanation is that the nitrogen gas, while it is inert, displaced gas that was previously dissolved in the oil mixture leading to a higher viscosity that way. One thing is for certain, and that is that there is gas that is dissolved in the oil at high pressure. Whenever a sample was depressurized and taken out of the vessel, gas would begin to bubble up out of the mixture making a frothy layer as seen in Figure 40. While at least part of it is dissolved nitrogen, there could be some gaseous hydrocarbons mixed in as well.

Figure 40 Oil mixture post-processing run with gas bubbling out of the processed mixture

From these experiments it was learned that the viscosity of a treated sample should be compared to a control sample that was exposed to the same temperature and pressure. The primary objective is to see if the microplasma ball reactor will work for heavy oil conversion, and if so what parameters produce the best results.

4.3.4 Pure Crude Oil Experiments

A ceramic reactor was machined so that processing could be done at high temperature and pressure without damaging the material. It can be seen in Figure 10. The reactor was designed to go inside of a pressure vessel that can be heated and controlled by a PID controller as seen in Figure 14. This allows for precise control over temperature and pressure of the reactor processing environment. The tank is pressurized to around 300 psig to keep produced liquid hydrocarbons from evaporating and heated to around 130 F to reduce viscosity for processing.

Because the pressure vessel is essentially a large oven the temperature can be set high enough that pure heavy crude oil can be used and the viscosity will still be low enough to allow the balls to move. From the results of the conductivity experiments seen in Figure 37 pure crude oil would reduce the efficiency losses from a high conductivity oil mixture.

For about 400ml of heavy crude oil, the process was run at 175F and 225psig. The total energy input was 200kJ/kg. Because the conductivity was low (about .05 mA/kV) the processing time was rather lengthy. The total processing time was 160 minutes. The post processing viscosity results can be seen below in Figure 41.

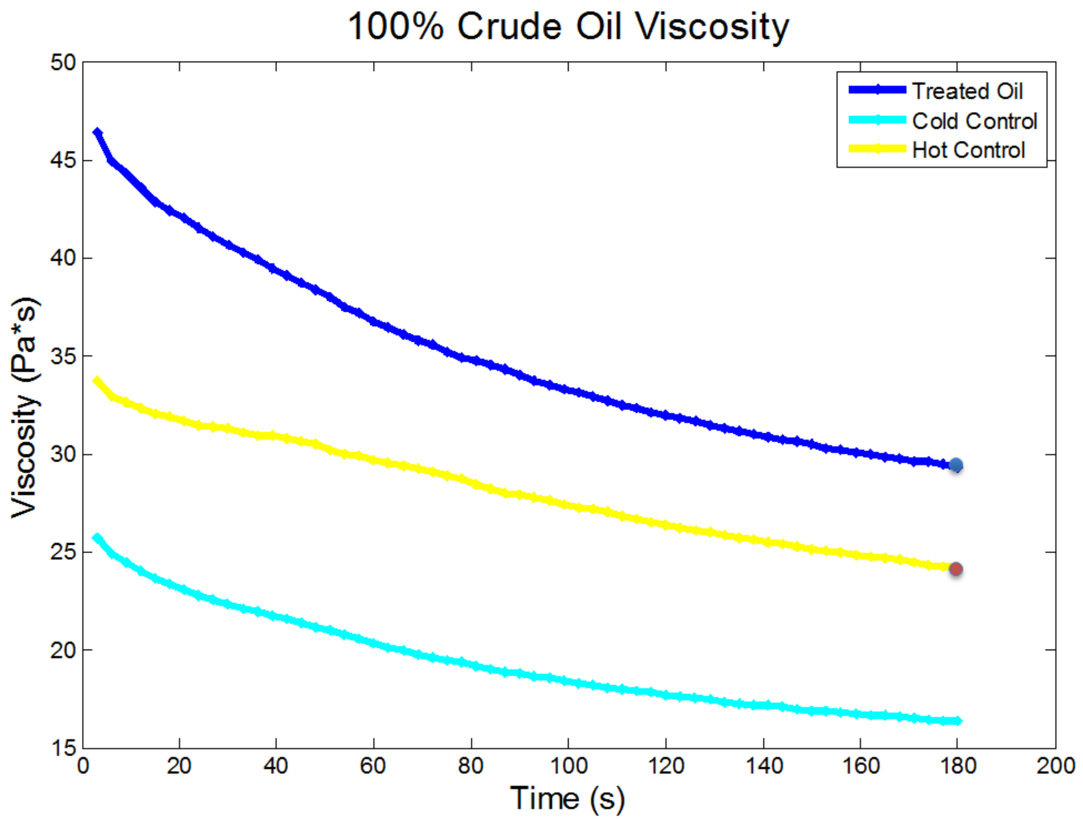


Figure 41 100% crude oil processing viscosity results where the treated oil is the sample that was processed, the cold control is the control sample that was left at atmospheric conditions and the hot control was an unprocessed sample that was inside the vessel chamber exposed to the same temperature and pressure as the treated sample

From processing compared to the hot control, there was a viscosity increase of about 20%. While there are less electrical losses due to the low conductivity of the pure oil, processing with increase the final viscosity without the presence of a hydrogen donor. For this reason processing experiments were done at a lower temperature but with some mixture of light oil with the heavy crude to serve as a hydrogen donor during processing.

4.3.5 Methane Bubbling Experiments

One possible way to still get around mixing the heavy crude oil with a light oil is to have a gas phase hydrogen donor. Since natural gas is something that is readily available in the field, methane was used as a hydrogen donor. A bubbler was setup to feed methane to the bottom of a bowl with the oil and reactor in it. The methane would bubble through the fritted glass on the bottom while the reactor was running. This was also done at high pressure and temperature. There was sporadic bubbling of methane through the oil because of how thick it was, and it was determined soon that these experiments were unsafe and were put on hold.

Prior to bubbling methane through the oil, nitrogen was used to pump the pressure vessel up to high pressure. The vessel was purged so that there was only a fraction of a percent of oxygen in the vessel. The exterior of the vessel was then thoroughly checked for leaks using soapy water. As a safety precaution there is a hazardous gas detector and alarm system setup in the lab to notify personnel of a leak before it becomes a serious problem. Only then was the vessel heated up and methane bubbled through. The only problem was that there was no way to quickly vent the chamber. The PVC exhaust pipe did not hold up to a sudden release of pressure from the chamber when tested with pure nitrogen. In case of emergency with the tank full of high pressure methane an emergency rapid release path would be necessary. Work is being done to install a chimney for this purpose. While bubbling methane through oil is a promising idea, safety is of primary concern.

4.3.6 Crude Oil Mixture Processing Experiments

The majority of work done processing heavy oils was done experimenting on processing crude oil mixed with some form of light liquid hydrocarbon which was either mineral oil or cycle oil. As previously stated, mixing light hydrocarbons in with heavy ones allows the processing temperature to be lower without sacrificing low processing viscosity. Light oils also provide a donor for hydrogen molecules during processing.

Crude oils were generally mixed with 30% mineral oil by volume, or 20-30% cycle oil by volume because the cycle oil was a slightly thinner mixture. Less light oil is preferable because it means a larger amount of heavy oil is being processed. Because the conductivity of the mixture is higher for these mixtures than for pure crude oil and processing energy input is desired to be close to the same, the processing time was shorter.

There are two main diagnostic methods used to determine if processing is taking place. The first is a visual check through the looking glass at the top of the pressure vessel. If the balls in the reactor are bouncing, the surface of the oil will shimmer. The other check is to see where the current changes non-linearly in the voltage current relationship. For the first type of crude oil mixture this non-linearity change happens around 9 or 10 kV as seen in Figure 42. The non-linear portion of the voltage current plot illustrates that there is an additional non-conductive current that is due to the carrying of charge by the balls as they begin to move. Two different types of heavy crude oil were used and some of the better results from each will be shared in this section. A table summarizing all of the heavy oil results will be provided in a following section.

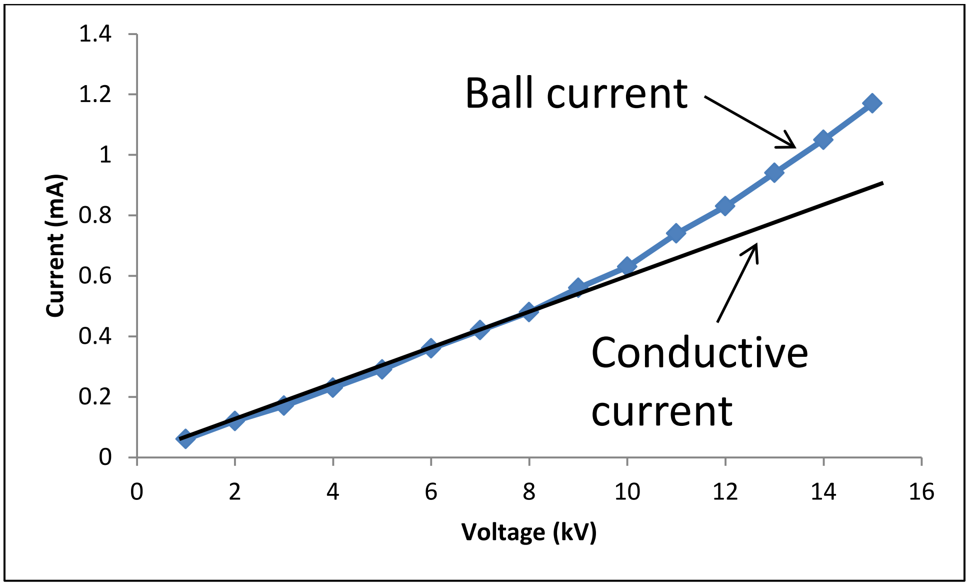


Figure 42 Voltage current relationship for mixture of 70% crude oil 30% cycle oil in ceramic reactor with the conductive and ball currents shown

While the voltage current relationship is valid initially, the conductivity of the oil can change predictably or fluctuate rather randomly. For this specific crude oil the fluctuations were seemingly random as seen in Figure 43. The exact cause for this seemingly random change in conductivity is unknown. It is possible that the mixture was not entirely homogeneous or there are other impurities in the oil. It does not seem to affect the microplasma processing because there is a noticeable viscosity reduction of about 17% which can be seen in Figure 44. Only 115 kJ/kg of input energy was used in order to see this noticeable viscosity decrease. The operating parameters for the vessel were 130F and 200 psig.

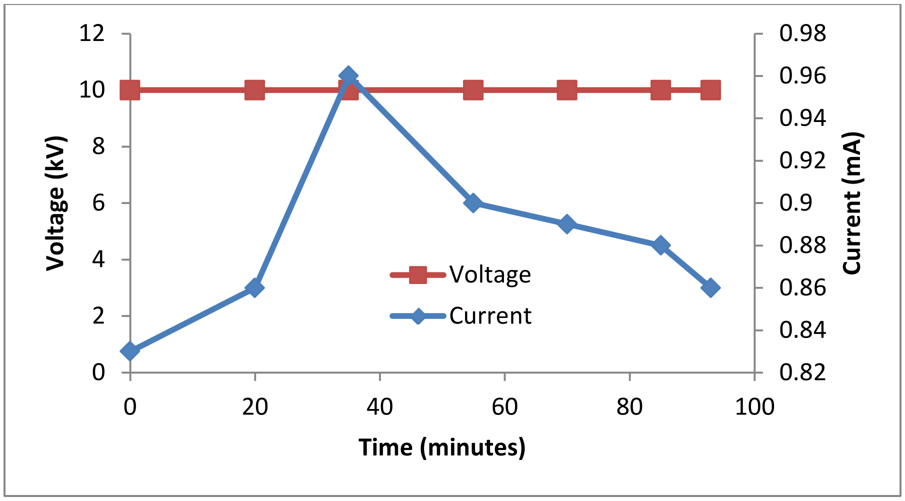


Figure 43 Current fluctuations processing 70% crude oil 30% cycle oil mixture at 130 F and 200 psig

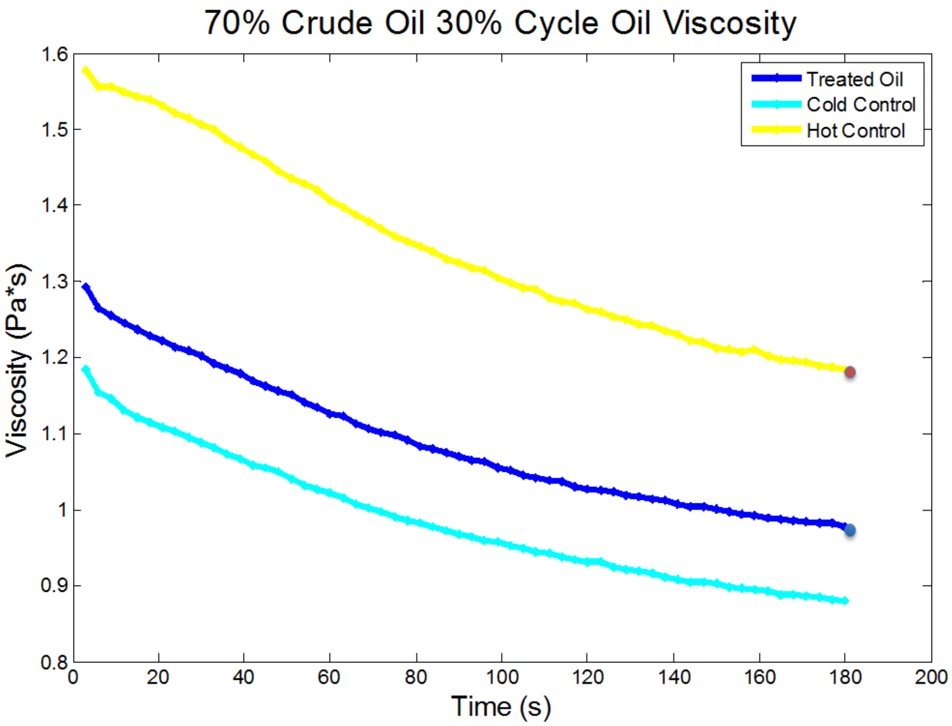


Figure 44 Viscosity reduction for 70% crude oil mixture with the treated oil being processed at 130 F and 200 psig with a total energy input of 115 kJ/kg. Cold control is left untreated outside the vessel and hot control is untreated but exposed to the same temperature and pressure.

While reduction in viscosity is important for decreasing the power required for transporting the crude oil by pipeline, it is not the objective of the processing. Viscosity reduction is a sign of a shift in molecular concentration away from heavy and complex hydrocarbon molecules and towards shorter and simpler ones. Figure 45 illustrates the results of a simulated distillation process of a processed heavy oil mixture. A process mimicking the full scale distillation process was performed on small sample sizes. The large peak representing mass fraction boiling off around 700 F is the mineral oil in the mixture being boiled away. The treated sample shows a higher mass fraction being boiled off between temperatures of 200-400F as well as a lower mass fraction being boiled off at higher temperatures (greater than 900F) than the untreated oil mixture and pure crude oil. This shift in mass fraction illustrates that not only was viscosity reduced through processing, but the composition of molecules in the oil has been permanently changed.

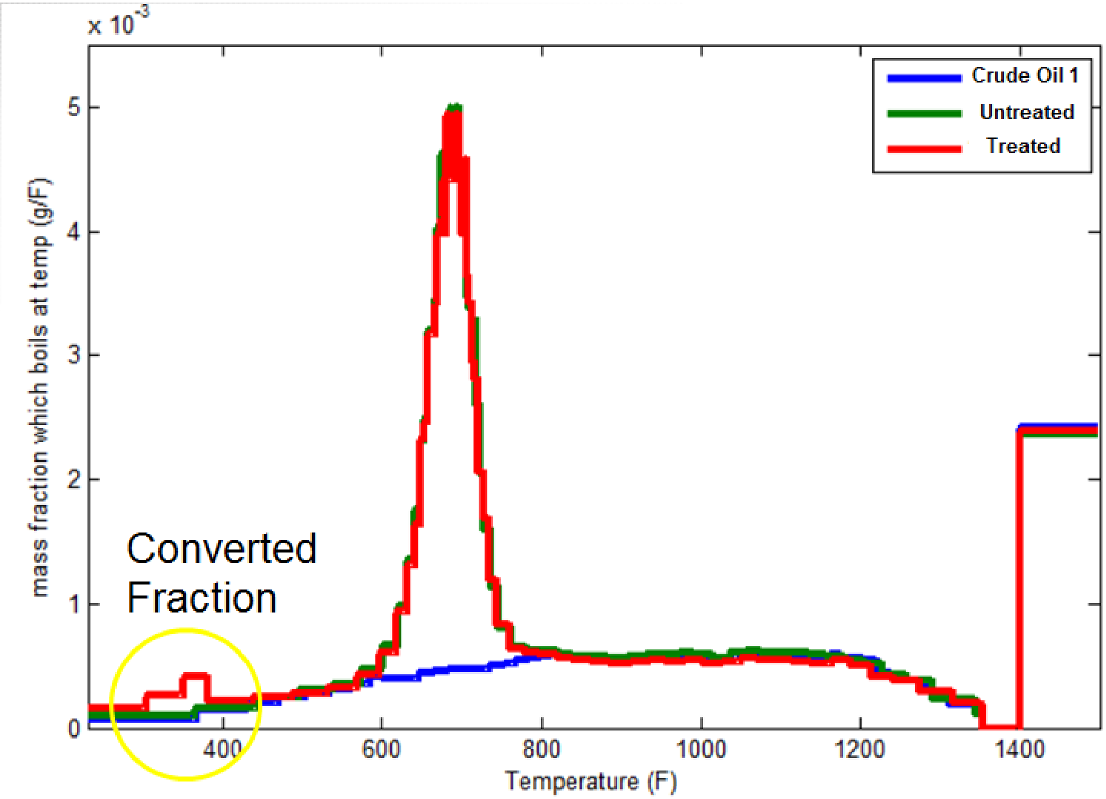


Figure 45 Simulated distillation of a treated crude oil mixture showing conversion of heavy mass fractions into lighter ones with the untreated sample being the mixture control and the treated being the mixture processed by the ball reactor

The second type of heavy crude oil is different from the first in that it was gathered from a different oil field. The composition is probably slightly different however the viscosities of the two oils were similar. This mixture used mineral oil instead of cycle oil in a 30% by volume composition. This mixture was more conductive as seen by the voltage current relationship in Figure 46. In addition, this mixture decreased rather predictably during processing as illustrated in Figure 47. For this type of heavy crude oil mixture, the conductivity is an indicator to the amount of processing that has taken place. This further illustrates the permanent change to the molecule size and distribution in the mixture.

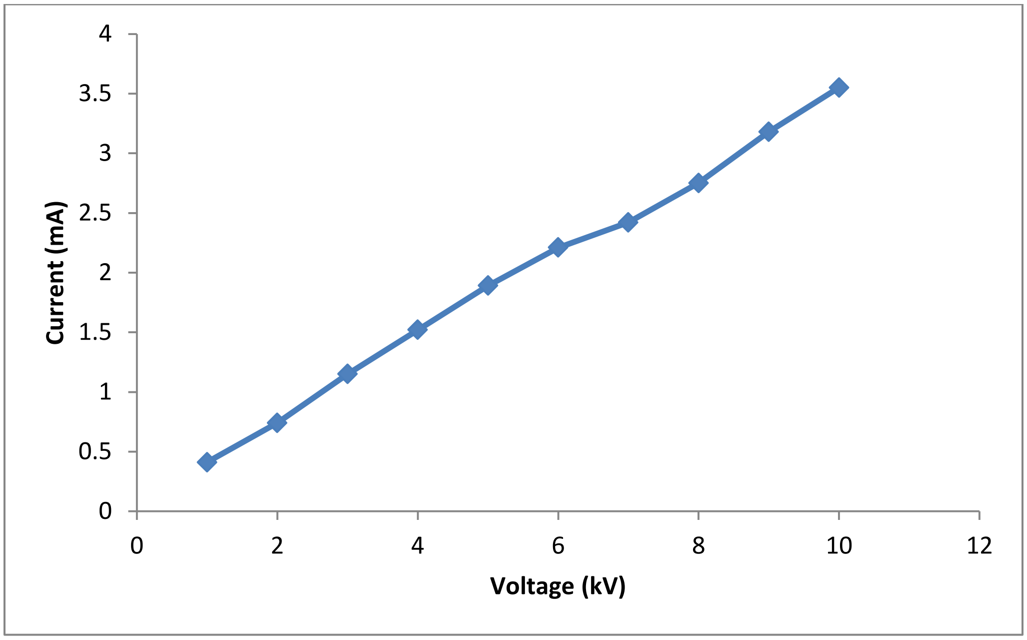


Figure 46 Voltage current relationship for higher conductivity crude oil mixture

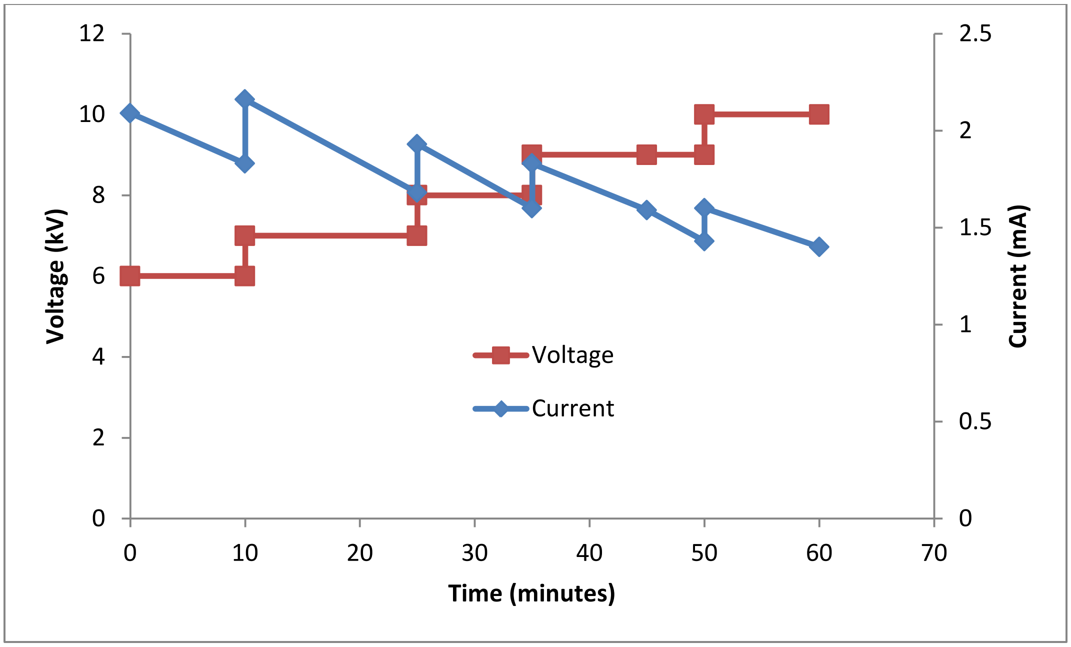


Figure 47 Voltage and current during the processing time for a heavy oil mixture

Because this mixture of crude oil was slightly thicker than the first, a slightly higher temperature of 150F was used along with a pressure of 200psig. Likewise, the total input energy was 115 kJ/kg. With these parameters the viscosity reduction was about 25% as seen in Figure 48. This crude oil mixture even had a lower processed viscosity than the original control not exposed to heat and pressure. It is possible that even more processing could have been done if additional energy was added. It is important to highlight again what the viscosity change represents. It is evidence of a permanent change in the hydrocarbon molecule size distribution in the oil. The average chain length is shortening and the C/H ratio is decreasing.

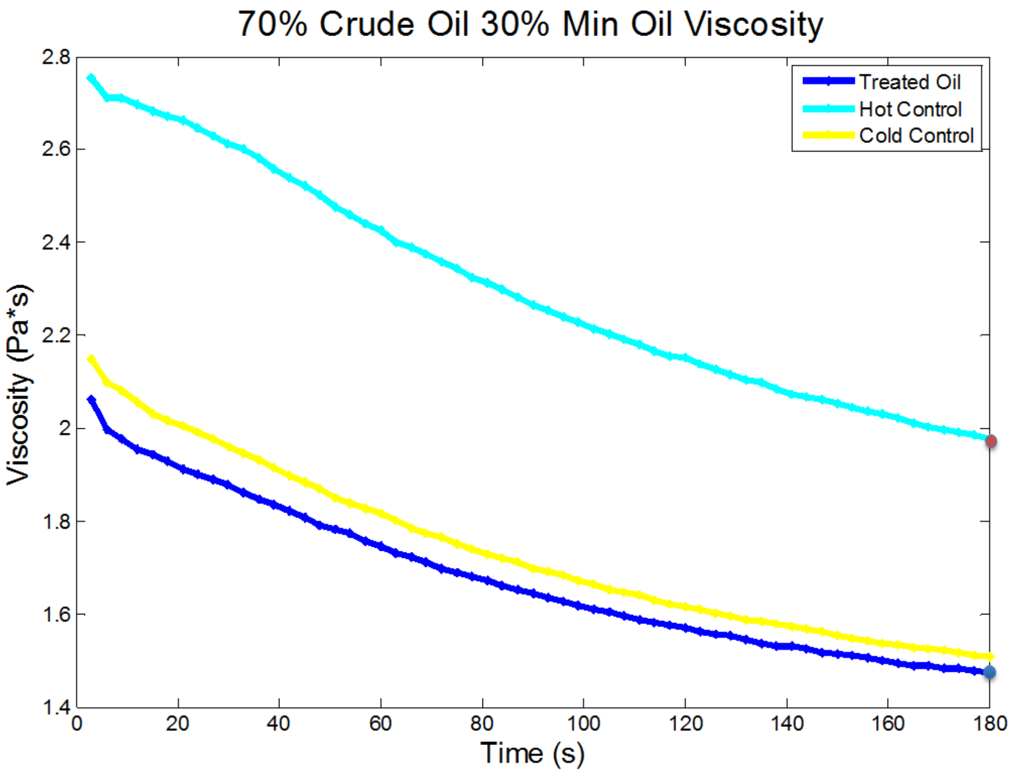


Figure 48 Viscosity reduction of crude oil and mineral oil mixture processed at 150F 200 psig for an energy input of 115 kJ/kg with the hot control being the untreated sample exposed to the same temperature and pressure as the treated one, and the cold control was just left at atmospheric conditions

As was mentioned previously, both of these are representations of better results. A range of different samples run at different temperatures and pressures can be seen in Table 6. This table isn’t a complete list, but it provides a broad spectrum of different processing parameters that were tried and gives insight into their effectiveness. In order to fully understand the effectiveness of processing heavy oils with the microplasma ball reactor extensive optimization experiments should be performed. The results below are a good basis to start with and evaluate the effectiveness of different parameters in the process.

Table 6 Summary of the viscosity changes in heavy oil mixtures at various processing parameters

Mixture	Pressure (psig)	Temperature (F)	Ein (kJ/kg)	Viscosity Change %
70% Crude1/ 30% MinOil	0	140	208	-16%
70% Crude1/ 30% MinOil	0	140	417	-31%
70% Crude 1/ 30% MinOil	0	140	883	-40%
70% Crude 2/ 30% MinOil	200	150	115	-25%
100% Crude 1	225	175	200	20%
70% Crude 1/ 30% Cycle Oil	200	130	115	-14%
80% Crude 1/ 20% MinOil	300	130	100	-8%
80% Crude 1/ 20% MinOil	300	130	150	-3%
40% VR/ 60% Cycle Oil	300	130	115	-20%

This summary of results sheds light onto which parameters are important in heavy oil processing. Higher pressure processing is more efficient than atmospheric pressure processing. Nearly the same viscosity reduction can be achieved with 55% of the energy input. This is done solely by keeping light hydrocarbons in the liquid phase, which keeps them around to be processed again. The temperature is kept as low as possible while still hot enough to allow the balls to move freely in the columns. From the atmospheric pressure experiments it can be seen that higher total energy produces diminishing returns in viscosity reduction. A logical next step would be to figure out at what energy does the viscosity change cease to happen or revers the change becoming more viscous. While the above table provides insightful information, it opens the door for a whole new set of experiments that could be run to further optimize this process.

4.3.6 Vacuum Residue Mixture Processing Experiments

The application for processing VR oil is nearly the same as the heavy crude. The desire is to decrease the C/H ratio and reduce the viscosity. Because VR is created in the bottom of a distillation tower in a refinery, it makes the most sense to mix it with the refinery cycle oil. As described earlier, the VR and cycle oil were mixed using the liquid nitrogen mixing technique. The mixture was 40% VR and 60% cycle oil by mass. This mixture was different than other heavy oil mixtures in that it was incredibly conductive as seen by the voltage and current graphs during the processing time which are seen in Figure 49. It is evident that the conductivity initially drops off rapidly and then starts to slow down as more processing takes place.

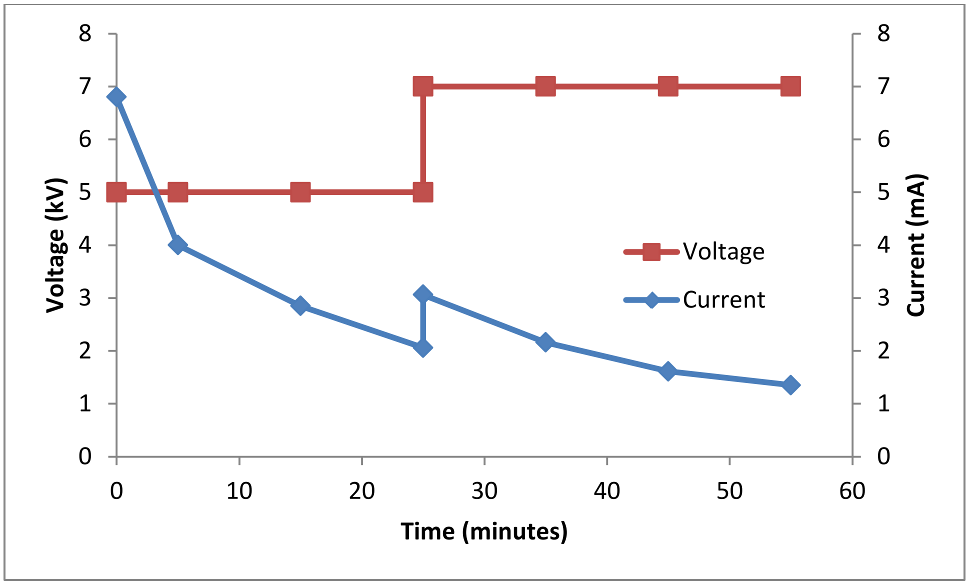


Figure 49 Voltage and current in the microplasma ball reactor while processing a VR mixture

The VR oil mixture was treated with the same energy input of 115 kJ/kg. The temperature was 130F and the pressure was kept at a slightly higher pressure than other samples at 300 psig. The results can be seen below in Figure 50 with a viscosity reduction of around 20%. With the case of the VR, the hot and cold controls are very close to the same viscosity. This might have to do with the fact that this oil has already gone through a refinery and been exposed to temperatures and pressures. Molecules have already been deformed and the lights in the mixture were nonexistent.

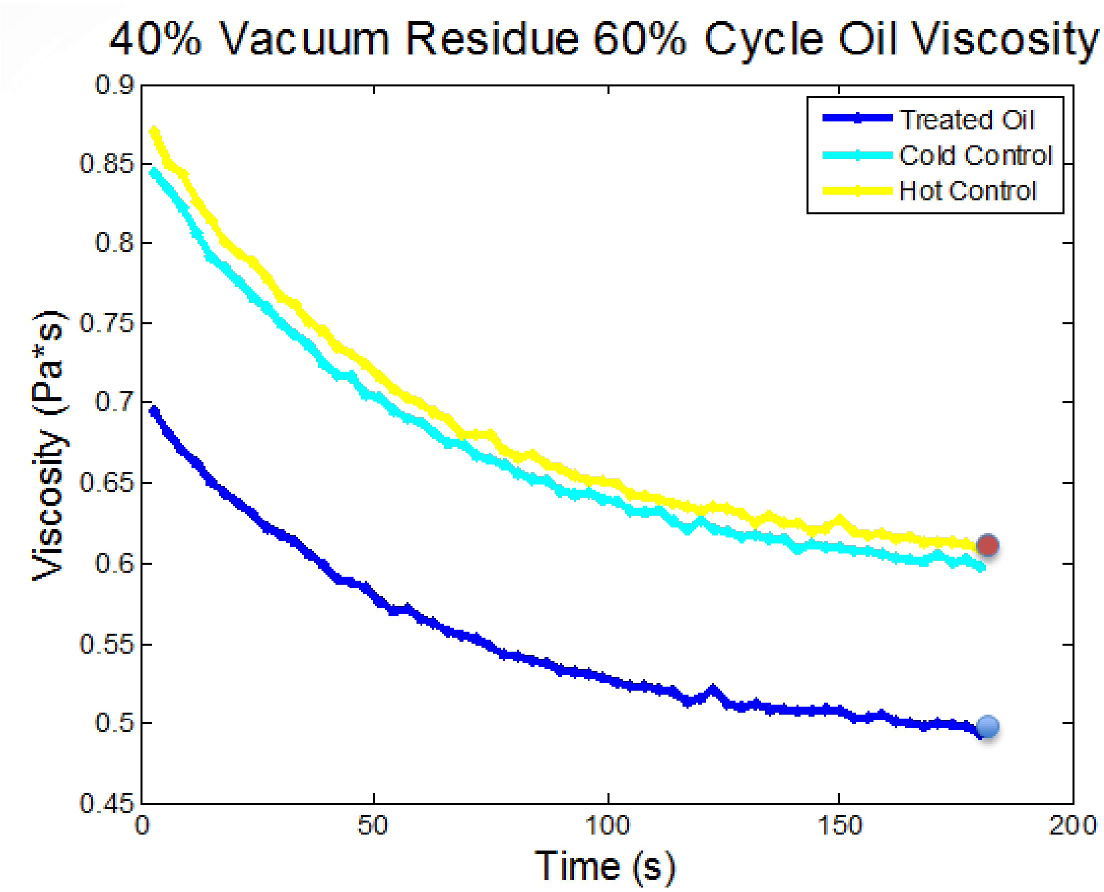


Figure 50 Viscosity reduction for VR oil processing in microplasma ball reactor at 130F 300psig for a total energy input of 115 kJ/kg with the hot control representing an unprocessed sample exposed to the same conditions as the treated sample and the cold control was held at atmospheric conditions

In order to test how well the microplasma ball reactor works processing the VR mixture a control experiment was done by removing the balls from the reactor and leaving the wire electrodes. In this way processing can only be done by electrically conducting through the mixture. There is no plasma discharge when there are no balls in the reactor. The same voltage vs time setting was used on the power supply as the processing with balls seen in Figure 49. The voltage and current were measured for both cases and the change in conductivity over the time of processing is plotted below in Figure 51. Although the case with balls should be more conductive because there is shorter difference for the charge to travel, the percentage change in conductivity is much higher in the case of processing with the balls. With the balls the drop in conductivity was 86% and the drop was 43% without the balls.

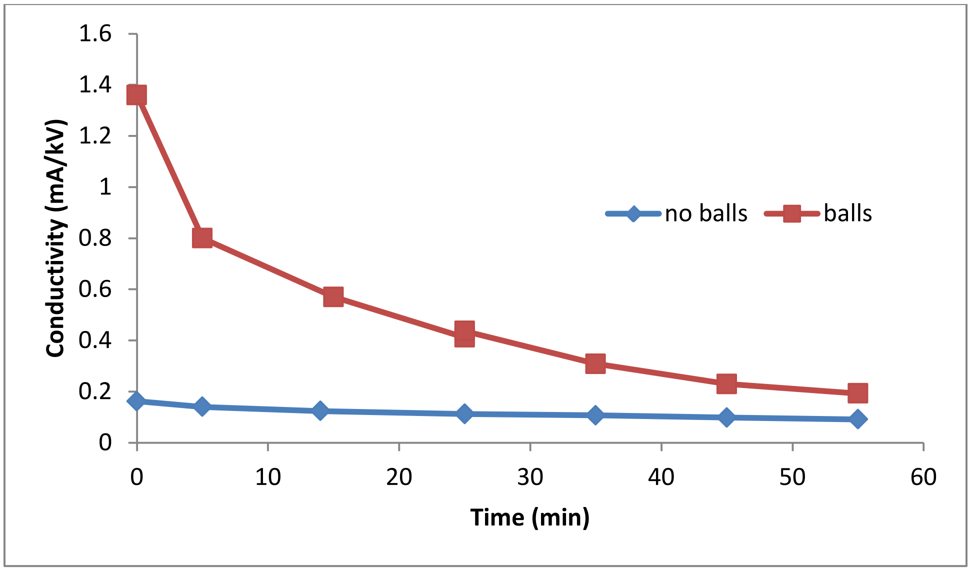


Figure 51 Change in conductivity of VR during processing with and without balls

One of the more puzzling results from the processing without balls is that the viscosity reduction before and after processing in both cases was around 20%. Unlike the heavy crude oil, the VR seems to be processed not by the plasma discharge, but by the movement of charge through the oil. This is known as electrochemical reforming and is a process that is not well understood.

The VR experiments show similar promise of using the microplasma ball reactor to the heavy crude oil experiments. There appears to be a slightly different method of processing in the case of the VR oil mixtures. The lack of light hydrocarbons mixed in helps with processing in this case because there are a higher percentage of target molecules available for cracking reactions.

5. CONCLUSIONS

The goal of this research was to use plasma technology to reform liquid hydrocarbons. This was specifically carried out by different versions of the microplasma ball reactor. Literature was reviewed in order to understand the mechanisms of chemical reactions taking place. For JP-8 processing the objective was to use the microplasma ball reactor to convert the liquid fuel into an LPG compound consisting mainly of C_3 hydrocarbons. The objectives for the heavy oil processing were broader. For all oil mixtures it was desired to shift the bulk of molecules in the molecular distribution from long chain hydrocarbons to short chain. This in turn decreases the C/H ratio, and the physical evidence of this is a lowered mixture viscosity. For this reason viscosity was used as a metric to determine how much desirable processing had taken place.

5.1 Summary of Work Accomplished and Findings

Literature was searched and it was determined how the research for this thesis was different from what had been previously done. Previous hydrocarbon conversion was almost all done to create hydrogen gas. Heavy oils for the most part have been avoided. Using very small energy discharges lighter hydrocarbons can be produced that are not hydrogen by doing non-equilibrium plasma chemistry. The microplasma ball reactor was developed for this purpose. The bouncing ball provided a small specific energy input, the rapid discharges led to an overall high power process.

The first thing that was done was the optimization of the bouncing ball in a column. The current density through the reactor was optimized in order to have the highest possible power input while maintaining a low specific energy input. Using this data, a prototype nylon reactor was created in Solidworks and printed using a 3D printer. The reactor chamber was then created so that it could be sealed and gas samples could be obtained from processing. The GC and MS were set up and calibrated. It was determined that input power is directly related to flow rate which gives an accurate model for scaling up the reactor size. It was also observed that the reactor was most efficient at producing C_3 hydrocarbons after the same batch of JP-8 had been processed for a higher total energy input. An interesting finding was that while the gas composition did not seem to change for different discharge energies, the amount of soot produced changed quite drastically.

For the heavy oil experiments, it was learned how to create different mixtures of heavy oil with mineral or cycle oil in order to obtain different conductive or viscous properties. Light oils in the mixture also served as hydrogen donors during processing. For the microplasma ball reactor experiments a mixture with a low viscosity and conductivity for processing was determined. Since these properties are generally inversely related, compromises were made. The oil mixtures had to be heated during processing in order to have a low enough viscosity. In some cases processing was successful and viscosity was lowered. It was determined that in order for light hydrocarbons to not be lost during processing the ball reactor processing should be done at a higher pressure than atmospheric.

A pressure vessel was used for processing heavy oil mixtures. A valve system was setup to regulate the pressure inside the chamber with nitrogen gas. Radiative heaters were installed and a high current temperature control system was developed for use with the vessel heaters to give precise control over the temperature and pressure in the chamber. In order to process at high temperature and pressure a more durable reactor was designed and machined from ceramic. Using this setup higher viscosity reduction was seen for a lower total energy input for the different mixtures of heavy oil. Not only did viscosity change, but also conductivity changed during processing for some of the crude oil mixtures, and especially the VR mixtures. It was discovered for the VR mixtures that there is also processing done without plasma discharges with only charge conducting through the oil to lower viscosity.

5.2 Conclusions

The microplasma ball reactor works for reforming JP-8 and for reforming heavy oils. When applying the microplasma ball reactor technology it can and should be optimized to each specific application. Specifically for JP-8 it was discovered that small cheap balls were the most important. They can be packed tightly and offer a higher current density that way. For heavy oil processing, a reactor with larger columns and bigger balls was needed to allow for ball movement in the viscous mixture. The material used to create the reactor needed to be resistant to heat, pressure, and corrosion in addition to being a dielectric.

For the JP-8 experiments, the maximum mass conversion efficiency of C_3 hydrocarbons was 13%, and the necessary size of a scaled up reactor with the necessary output for practical use was determined to be 1.7 m^3 and it would contain 10.5 million individual columns. Using a microplasma ball reactor is an alternative to traditional plasma discharge processing options for fuels that allows for gaseous hydrocarbon products to be made without syngas production. An even smaller unit discharge, or a smaller energy per pulse, should allow a shift in the primary produced molecules away from methane and ethylene toward propane and butane.

From the heavy oil processing experiments it can be concluded that a pressurized processing environment can double the energy efficiency of conversion. Because viscosity is affected by average chain length of hydrocarbons, it is a valid indicator for the amount of processing done to a mixture. Different types of crude oil or VR have different molecular distributions and therefore each react to processing slightly differently. Some mixtures are more conductive than others or more or less viscous. A specialized process should be developed for each individual type of oil.

5.3 Future Work

For the JP-8 experiments it would be helpful to learn exactly why different amounts of soot production can equate to the same amount and composition of gas production. The exact mechanisms of the chemical reaction should be studied more to determine what products are being produced and how they are being made. A more firm understanding of how energy per pulse affects the chemical reactions taking place in the reforming process would be helpful. The next step however would be to make an even bigger prototype reactor to verify that the linear scaling holds true in a reactor with thousands or tens of thousands of balls instead of hundreds.

For the heavy crude oil mixture processing, a full optimization study should be done in order to determine optimum processing temperature, pressure, and voltage. The optimum total energy input is important to make the process efficient. An apparatus should be created so that methane can be safely bubbled through the oil at high pressure. The advantage of this is that pure heavy crude oil can be used, and the hydrogen donor methane is a compound found in abundance at well sites. For the VR mixtures experiments should be done to determine how the conductivity of a mixture changes with the amount of processing. It should also be determined how conducting through the mixture reduces the viscosity, and if the metal balls and microplasma discharges help in any way with processing.

In regards to changing the microplasma ball reactor, work has been done in order to adapt the reactor to use AC instead of DC. Though it is not detailed in this thesis, the use of AC helps to get rid of the conduction inefficiencies experienced by the traditional DC reactor. In addition, the ball does not have to move as far between discharges leading to reductions in inefficiency due to viscous drag losses in the fluid. The use of an AC microplasma ball reactor could be instrumental in increasing the energy cost efficiency of the process.

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