Preliminary results for Hydrocarbon conversion induced by submerged plasma

Kunpeng Wang¹, Shariful Bhuyian¹, Md. Abdullah Hill Baky¹, Christopher Campbell¹, Howard Jemison² and David Staack¹

¹Department of Mechanical Engineering, Texas A&M University, College Station, TX, USA ²LTEOIL LLC, 2929 Allen Parkway 200, Houston, USA

Abstract: Electrical discharge was generated under liquids with a carrier gas flow. Bubbles are formed in the spark gap and electrical breakdown happens after high voltage was applied between two electrodes. Plasma interacts with surrounding liquids on the interface and the interaction is able to produce new hydrocarbon products by converting original hexadecane molecules. After plasma treatment with 500 kJ/kg specific energy input, 7% conversion to lighter fractions as chain scission products and about 3% conversion to heaver fractions as chain growth products were both found in treated samples.

Keywords: electrical discharge, bubbles, breakdown, plasma, transforming, interface.

Introduction

Refining technology used in oil industry such as thermal cracking, catalytic cracking and hydrocracking have been widely applied to convert upgrade heavy oils [1-3]. These methods are characterized as thermal methods and operate under thermal equilibrium conditions which require high temperature and high pressure[4]. But they are typically capital intensive, highly complex, and require very large scales for economic justification[5]. Non-thermal methods such as high energy electron beam irradiation and nonthermal plasma (NTP) processing could operate at nonequilibrium conditions and represent much higher efficiency[6-10]. Especially non-thermal plasma, due to many of its inherent advantages over thermal method, has been researched and developed as a new method for liquid processing including wastewater purification and fuel reforming[11]. Non-thermal plasma is best known for its unique nature that allows to have large varieties of reactive species (high energy electrons, ions, radicals) at different energy states within a small region, while the bulk material inside which plasma was generated is still at or close to room temperature.

Non-thermal plasma to convert or upgrade heavy oils is a relatively new method. Different type of non-thermal plasma have been investigated for the potential application in this area. A gliding arc reactor was designed to convert gasoline into hydrogen rich gas for fuel applications[12]. The author studied the influence of operating parameters (pressure, temperature, gas flow rates) on the reformer efficiency and the composition of the produced gases. Yury Novoselov invented a process for cracking liquid hydrocarbons by pulsed electrical discharge using a submerged high voltage spark gap in liquids[13]. Significant hydrocarbon conversion in the range of C10 to C22 was reported in this patent. Jahanmiri investigated a pulsed catalytic dielectric barrier discharge (DBD) reactor for cracking hexadecane and naphtha[14]. Production of lighter hydrocarbons from converting those model hydrocarbons was studied with different catalysts and pulsing frequency. Heavy oil upgrading in a semicontinuous system was proposed by Hao, who combined conventional thermal cracking and a cylindrical dielectric barrier discharge (DBD)[15]. The author compared the treated oils when plasma was on and off and separated the net effect plasma. Different carrier gas was tested and effect of carrier gases on hydrocarbon fraction distribution was evaluated. They found hydrocarbon and methane both showed a high reactivity in the heavy oil processing and helped increase the yield of light hydrocarbon fractions.

In this paper we investigated a discharge geometry similar to that of Novoselov, using a low energy nanosecond pulsed discharges to generate reactive species at the gas liquid interface submerged in hydrocarbon liquid. This configuration is capable of achieving noticeable conversion at relatively low specific energy input.

Experimental Design and Setup

The schematic of experimental setup was shown in Fig. 1. Carrier gas was injected into a spark gap between two electrodes submerged in liquid hydrocarbon in a discharge chamber. Chamber was cylindrical made of quartz glass which allows taking high speed video and emission spectra in the discharge process. Top electrode is a grounded stainless steel rod with 3/8 inch OD. Bottom electrode is a capillary with ceramic sheath with two primary functions: serving as the high voltage electrode and allowing carrier gas to form bubbles in the liquid between the two electrodes. In this case a capillary tube with 0.75mm ID was insulated with a ceramic tube as the bottom electrode. Outside the chamber it has a Tee shape with two inputs for high voltage and carrier gas. Reactor body is aluminium with all fittings made of stainless steel. It has a cartridge heater and thermocouple which allows for controlled high temperature processing of heavy oils and crudes up to 250°C. Reported here is ambient temperature processing of a lighter hydrocarbon.



Fig. 1. Schematic of the Experimental Setup

DC power supply (Glassman SERIES FC) with maximum 50kV and 2.5mA output was used to power the spark gap. A 1.5 M Ω external resistor in series then a capacitance in parallel to the reactor were used to form a RC circuit. The installed capacitance was 20 pF for this study. Stray capacitance (<10 pF) also contributes to energy storage. A methane and hydrogen gas flow mixture to the reactor were controlled by two Alicat Scientific flow controllers. Voltage and current from the power supply were gathered with National Instruments device USB 6341. Power of this reactor was calculated based on the voltage and current signals. The current trace was analysed to know when discharge events occurred. The voltage on the capacitor was calculated from the power supply voltage and voltage drop on the resistor. Energy stored on the capacitor was assumed (based on independent high fidelity voltage, and current measurements) to be the energy release per discharge event. Specific energy (kJ/kg) into the oil was calculated from the accounting of energy per pulse for each pulse and mass of the treated sample. It was at 500 kJ/kg for this plasma treatment process. This energy was chosen because it corresponds to about 0.85-2.5 \$/bbl of liquid which is an economically viable processing cost. GC-FID analysis with method D2887 was used to study products in treated oil samples. GC-MS analysis was performed at the Chemistry Mass Spectrometry Facility in the Chemistry department at Texas A&M University. ATR-FTIR in Material Characterization Facility at Texas A&M University was used to study chemical bond change.

The actual experimental setup was shown in Fig. 2. Note that two holes were produced on the reactor body to fit a cartridge heater and thermocouple when processing samples at higher temperature. Two ceramic cylinders with threads for an insulated compression connection between the top and bottom part of the reactor.



- 1. Aluminium plate
- 2. Fitting
- 3. Ceramic connector
- 4. HV electrode
- 5. grounding electrode
- 6. Holes for heater

Fig. 2. Actual Experimental Setup.

Carrier gas flows into the spark gap and form bubbles which move at a relatively constant speed from the bottom electrode to the top electrode. There is liquid film between two adjacent bubbles and the thickness of the liquid film depends on the gas flow rate, liquid viscosity as well as its surface tension. High voltage was applied on speak gap and caused electrical discharge through both the bubbles and liquid film. Plasm liquid interaction was believed to happen in the discharge region and bring about any chemical change to the sample. Important parameters in this experiment include but not limited to energy per pulse, specific energy input and bubble size. High purity (>99%) n-hexadecane was tested in this spark gap reactor. Pure hexadecane has a boiling point larger than 500F at atmospheric pressure and low viscosity at 25C. It is a clear liquid and odourless.

Submerged spark gap operation characteristics inside liquid hydrocarbons were studied by varying multiple experimental parameters. Discharge gas composition was believed to affect products distribution in processed samples, for example higher hydrogen composition will suppress the production of solid products. Gas flow rates might change the bubble size and the plasma liquid interface, therefore change the plasma liquid interaction. Spark gap distance determines the number of bubbles in the gap for a constant bubble size. Multiple bubbles are preferred in the gap for a few reasons: discharges in multiple bubbles are more statistically consistent; multiple bubbles compared to one bubble provides larger gas liquid interface which favor the gas liquid interaction; discharge in multiple bubbles might prevent gas in bubbles from being overheated and generating undesired species like solids. Pulsing energy is another important parameter that significantly affects the discharge properties and products. It is controlled by changing the capacitor size as well as the breakdown voltage. Pulsing energy affects the discharge properties and products by changing the temperature of plasma species and kinetics of reactions, thus to favor or un-favor a certain reaction. Specific energy input (SEI) to oil sample is not an independent parameter and depends on the discharge power and processing time. SEI was estimated for each test. Table 1 lists the experimental parameters and their range in one experiment with plasma.

Tuete II Zaperintenta I arameters.		
parameters	Test	Control
gas flow rate (LPM)	0.05	0.05
capacitor (pF)	20	NA
H2, %	10%	10%
Plasma Energy kJ/kg	500	0
Temperature, C	Room	Room
Duration, hr	3	3

Table 1. Experimental Parameters

Results and Discussions

Voltage and current from the power supply were analysed with LabVIEW device USB 6341 at 100 kHz. Each current peak was analysed to study its height, width and time. Breakdown happens before the peak current by a certain amount of time. The value of a time delay like this is equal to the width of the current peak (w). Breakdown voltage was equal to the difference between the total voltage and voltage on the external resistor. Breakdown voltage was then used to calculate the pulsing energy with known capacitor size by using:

$$E = \frac{1}{2}CV^2 \tag{1}$$

With known breakdown voltage and number of pulses, we were able to estimate the power of the spark gap as well as the specific energy input to the sample. Mass loss after the experiment was compared to the control sample. Mass loss from plasma treated sample was 3.38% of total weight, much higher than 0.7% from the control sample. This indicates that plasma in liquid help create more HC species which will escape the reactor and those species are very likely hydrocarbons lighter than the original hexadecane molecule.

Appearance of treated sample showed significant change compared to the raw sample as showed in Fig. 3. Raw mineral oil is a clear and odorless liquid. Treated mineral oil became brown and with some precipitates. The estimated weight of precipitate was about 1%.



Fig. 3. Appearance of Samples (raw and treated)

GC-FID analysis was used to study the hydrocarbon distribution as well as its change after plasma treatment. Distribution was shown in Fig. 4. More than 96% of hydrocarbon species in both the raw and treated samples were boiled off before 16 minutes. Less than 1% was found before 10 minutes and about 2-3% were distributed after 17 minutes.



Fig. 4. Hydrocarbon Distribution in Samples

Distribution was shifted significantly after plasma treatment and the change was shown in Fig. 5. Treated sample had about 7% gain on lighter species before the 16^{th} minutes compared to the raw sample. This number agrees with the distribution loss after the 16^{th} minutes. It indicates that plasma treatment converted heavier fractions to lighter fractions in hexadecane.



Fig. 5. Hydrocarbon Distribution Change

GC-MS analysis provides further information on products produced by discharges in the treated samples. Specifically we can evaluate the reduction of original hexadecane peaks and the creation of new products. Both the raw and treated sample had three repeating runs to reduce uncertainty. Fig .6 showed the hexadecane peak area change after plasma treatment. Hexadecane peak areas in the treated sample were smaller than that in raw sample by about 20%.

Reduction of hexadecane molecules was due to conversion to other molecules. Since thermodynamic state (ambient pressure and temperature) do not support and chemical reactions, conversions were induced by nonequilibrium plasma in the liquid.



Fig. 6. Hexadecane Peak Change

FTIR analysis was performed on different samples to analyse carbon-carbon and carbon-hydrogen bonds change induced by plasma. Octene was used as a reference to qualitatively study double bond change in the treated sample. Fig. 7 shows the results. IR spectra of raw hexadecane and treated hexadecane are very identical. Octene peaks corresponding to 917 and 1004 cm⁻¹ are for H - C = bending. Octene peak at 1640 cm⁻¹ is for C = C stretching and peak at 3083 cm⁻¹ corresponds to H - C = stretching. Those peaks were not found in treated sample, which indicates that no significant amount of olefins were made in the process.



Conclusions

Electrical discharge was generated by injecting carrier gas into a spark gap submerged in liquids. The discharge was able to change hydrocarbon distribution in the sample by converting original molecules to new molecules.

Discharges were controlled and monitored through voltage and current signals from the power supply. Breakdown voltage, spark gap power and specific energy were estimated in real time bases on those signals.

Both GC-FID and GC-MS were used to analyse products after plasma treatment. GC-FID showed significant conversion of the hexadecane molecules to new molecules that represent lighter fractions in the sample. GC-MS indicated that more than 20% of hexadecane was consumed. This was achieved with only 500 kJ/kg energy input, which indicates great process economics. FTIR results did not show any olefins in the products. Based on the results this method of creating a plasma under liquid represent a hydrocarbon cracking process, which could be used as a refining method for heavy oil conversion or upgrading. Compared to thermal methods which only occur at high temperature and high pressure with thermodynamics equilibrium conditions, this method is dictated by non-equilibrium and can process hydrocarbons at ambient conditions.

Acknowledgements

We thank LTEOIL, LLC for financial support; Dr. Yohannes Rezenom for GC-MS analysis and my colleagues: John Lassalle, Xin Tang and Matthew Burnette in the Plasma Engineering and Non-equilibrium Processing Lab for meaningful discussions.

References

- [1] Sadrameli SM. Fuel 2016;173:285–97.
- Pines H. The Chemistry of Catalytic Hydrocarbons Conversions. Academic Press; 1981.
- [3] Joshi JB. Ind Eng Chem Res 2008;47:8960–88.

- [4] Olah GA, Molnar A. Hydrocarbon chemistry. vol. Volume II: 2003.
- [5] Chen Y. 10 Th Int Conf Circ Fluid Bed Technol Fluid Technoloy-(CFB -10) 2011;7:58–85.
- [6] Novoselov Y. Process for Cracking of Liquid Hydrocarbon Materials by Pulsed Electrical Discharge and Device for Its Implementation, 2014.
- [7] Gutsol A, Rabinovich A, Fridman A. J Phys D Appl Phys 2011;44.
- [8] Wu G. Ind Eng Chem Res 1997;36:3498–504.
- [9] Wu G. Ind Eng Chem Res 1997;36:3498–504.
- [10] Földiák G. Radiation chemistry of hydrocarbons. Akad. Kiadó; 1981.
- [11] Bruggeman PJ. Plasma Sources Sci Technol 2016;25:53002.
- [12] Paulmier T. Chem Eng J 2005;106:59–71.
- [13] Novoselov Y. Process for Cracking of Liquid Hydrocarbon Materials by Pulsed Electrical Discharge and Device for Its Implementation.
- [14] Jahanmiri A. Chem Eng J 2012;191:416–25.
- [15] Hao H. Fuel 2015;149:162–73.