

CHEMICAL REACTION INDUCED BY DISCHARGE PLASMA IN SUB- AND SUPERCRITICAL FLUIDS

Motonobu Goto*, Mitsuru Sasaki, Tsuyoshi Kiyari, Tao Fang, Bhupesh C. Roy, Takao Namihira, Hidenori Akiyama, Masanori Hara

Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan
E-mail: mgoto@kumamoto-u.ac.jp, FAX: +81-96-342-3679

Abstract

The generation of non-thermal plasmas was studied under supercritical conditions. This is interesting in view of both the basic phenomena involved and of potential industrial applications. When supercritical fluids are combined with discharge plasma they develop unique characteristics, including an enhanced chemical reactivity. This is the motivation for investigating the generation of discharge plasma in supercritical CO₂ and subcritical water. In this study, breakdown voltages were measured in CO₂ in order to generate electric discharges in near-critical fluids. The experimental data show that the breakdown voltage increased smoothly up to the intersection points, but beyond these points the rates of increase of the breakdown voltage are different. This phenomenon can be explained with the help of pressure-density curves of carbon dioxide at a constant temperature. In addition, the generated plasma in supercritical CO₂ and subcritical water was applied to several chemical reactions. The alpha conversion of tocopherols and transesterification of soybean oil with methanol were investigated. In addition, we explored the possibility of replacing catalysts with plasma in supercritical CO₂. The plasma generated in sub-critical water was applied to the reaction of phenol.

1. Introduction

The two main reasons for the considerable interest in supercritical fluids (SCFs) are that they are generally non-toxic and inexpensive, and that they have many attractive properties. These properties differ from the typical properties of gases and liquids, since they are intermediate between those two extremes. This makes them indispensable as extraction and reaction media since they have liquid-like densities and gas-like viscosities coupled with diffusion coefficients that are higher than those of liquids. These properties contribute to enhanced mass transfer, while their high thermal conductivity can be exploited to achieve high heat transfer. In addition, their properties can be manipulated by varying the pressure and temperature [1]. In view of these unique characteristics of SCFs, it is widely anticipated that subjecting an ionized state such as a plasma to supercritical conditions may result in unique characteristics and reactions that differ from those of a normal plasma in the gaseous state. Furthermore, the high-energy electrons, ions, and radicals that are generated when a plasma combines with supercritical fluids may generate new reaction fields, leading to effective pollutant oxidation for both homogeneous and heterogeneous reactions. It is thus important to make a systematic study of the pre-breakdown phenomena of electric discharges in SCFs before generating discharge plasmas effectively in sufficiently large reaction volumes before commencing. Generation of a micrometer-scale discharge in an SCF environment has been reported [2]. In the same study, a unique phenomenon was discovered, namely a minimum breakdown voltage existing near the critical point, which is probably caused by an unstable cluster in the SCF. On the other hand, *Lock et al.* initiated pulsed corona discharge under supercritical conditions, and reported that the breakdown voltage for a wire-in-cylinder configuration is three times lower than estimates based on Paschen's law due to the large inhomogeneities in the density of the supercritical fluid near the critical point [3]. Investigation of discharge phenomena in supercritical fluids is an underdeveloped field, and the pre-breakdown phenomena are not well understood. In this present study, carbon dioxide (CO₂) was selected as the medium for plasma production because it is non-toxic, non-flammable, readily available, environmentally benign, and has a low critical temperature (304 K) and pressure (7.38 MPa). The

breakdown voltages were measured in CO₂ in the pressure range 0.1-14 MPa and at temperatures of 298 K and 313 K by applying a negative DC voltage in order to characterize the electric discharges in supercritical CO₂. Subcritical water was also used as the medium. The ultimate goals of this research are to generate discharge plasmas in sufficiently large volumes that they can be used in various industrial applications, and to design a reactor with discharge plasmas in supercritical fluids.

2. Experimental

2.1. Experimental materials

CO₂ was supplied from Uchimura Sanso Co. Ltd. (Osaka, Japan) with a purity of 99.97%. Methanol (with a purity of $\geq 98\%$) and soybean oil were obtained from Wako Pure Chemical Industries Inc. (Tokyo, Japan). 57% tocopherol concentrate was supplied by Kaidi Fine Chemical Industries, Ltd., Wuhan, Hubei Province, China.

2.2. Apparatus and procedure

2.2.1. Apparatus for generating plasma under supercritical conditions

Figure 1 shows a schematic diagram of the test reactor for plasma production. It has inspection windows through which continuous monitoring was performed. The test reactor is made of stainless steel (SUS316) having a compressive strength of 30 MPa. The total volume of the reaction cell is 1300 mL. A power lead was introduced through the center of a long bushing made of peak resin, and the annular space was sealed with double o-rings placed around its outer surface to prevent air leakage. Liquid CO₂ from a cylinder with a siphon attachment was passed through a cooling head (about 268 K) of a high-pressure pump (PU-2086 Plus, Jasco) to the test reactor. A thermocouple and a backpressure regulator were used to control the temperature and the pressure of the test reactor, respectively. After the experimental temperature and pressure were achieved, the CO₂ medium in the test reactor was maintained under those conditions overnight. Then DC power was applied to produce electric discharges at a constant temperature. The breakdown voltages for the production of electric discharges were measured for pressures in the range of 0.1 to 14 MPa at each experimental temperature by removing CO₂ through the backpressure regulator. The electrode configuration consisted of a point and a planar surface. The point was made of tungsten and it was used as the negative electrode, while the planar surface was made of stainless steel and it was the positive electrode. This configuration produces a non-uniform electric field. The electrode gap was 200 μm . A voltage was applied to the negative electrode using a high-voltage stabilization DC power supply (HAR-50R0.6, Matsusada Precision Inc., Japan) that was controlled by a function generator (SG-4115, Iwatsu, Japan) at a rate of 2.5 kV/s. The breakdown voltage and the current were respectively measured using a high-voltage probe (EP100K, Pulse Electronic Engineering Co. Ltd., Japan) and a current transformer (4997, Pearson Electronics, Inc., USA) that were connected to a digital oscilloscope. The corona onset voltage was measured using a photomultiplier (No. 722, Atago Bussan Co. Ltd., Japan) coupled with an optical cable at 15 MPa and 313 K on trial basis. The interval between successive electric discharges was set at about 2 min in order to ensure that the CO₂ medium was in a steady state. Similar procedure was used for the experiments in subcritical water.

2.2.2. Application experiment using the plasma generated in supercritical CO₂ and subcritical water

The test cell was charged with 4 ml of either 57% tocopherol (Vitamin E) concentrate or soybean oil and a 20 ml methanol. This system was then treated with about 10,000 plasma discharges generated across blade electrodes with a gap of 1.7-1.8 mm in supercritical CO₂ at 18 MPa and 313 K. For the reaction of phenol in subcritical water, water and phenol was charged in the cell and plasma discharge was applied.

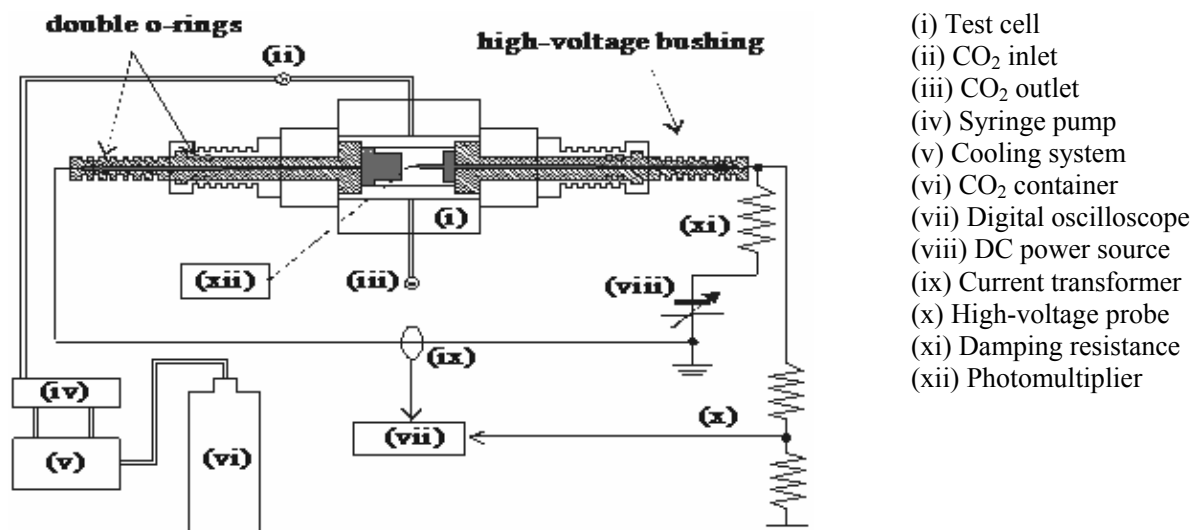


Figure 1. Schematic diagram of the experimental setup for supercritical CO₂ system

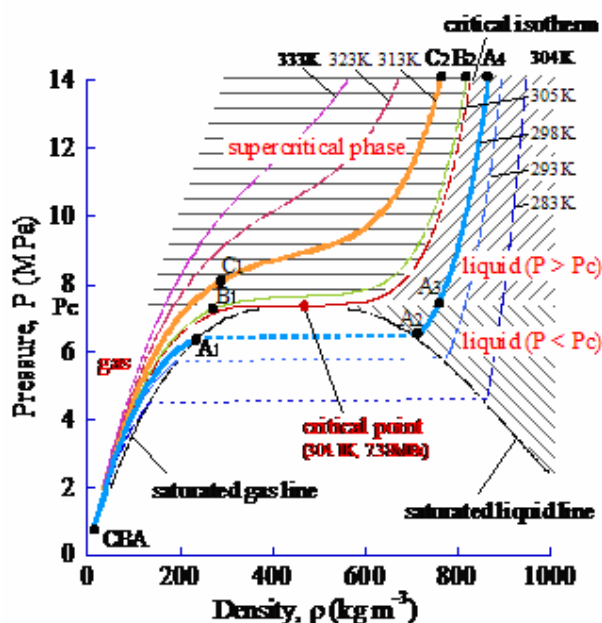


Figure 2. Pressure-density diagram of CO₂

3. Results and discussion

3.1. Pressure-density curves for CO₂

Figure 2 shows the pressure-density curves for CO₂ for the temperature range 283-333 K. In this figure, the bold lines at 298 and 313 K are the experimental temperatures for the production of electric discharges. These curves were calculated using the equation of state and they demonstrate the characteristics of electric discharges [4]. Ionization in gases and liquids is strongly related to the mean free path, which is proportional to density of medium. However, the phenomena are not well clarified in a supercritical medium. This figure shows that the curves above and below the critical isotherm have different behaviors with change in temperature. The area between the upper-right side of the saturated curve and the right-hand side of the critical isotherm represents liquid. However, from the viewpoint of electric discharge, it would be more appropriate to describe the areas above and below the critical pressure line as representing high- and low-pressure liquids, respectively. This distinction may help to explain the mechanism of the breakdown process. In Fig. 2, the curve of 298 K below the critical pressure in the gas phase intersects the saturated gas line at point A1 and then intersects the

saturated liquid line at point A2. It then moves upward through the low-pressure liquid region to the high-pressure liquid region. On the other hand, the curve of 313 K passes from the gas phase to the supercritical phase above the critical point.

3.2. Densities and breakdown voltage

The density dependences of the breakdown voltages at 298 and 313 K are shown in Figs. 3a and 3b, respectively. These figures reveal that the breakdown voltages increase smoothly up until the intersection points, but beyond these points they have different rates of increase. This characteristic can be explained with the help of the CO₂ pressure-density curves at different temperatures due to the different phase changes shown in Fig. 2. The abnormal changes in the breakdown voltages found near the boundary lines of 298 K and 313 K may be due to the density fluctuations at these conditions.

The density was calculated for the experimental conditions using the equation of state [4]. In Fig. 3a, the breakdown voltage in the gas phase conforms to the density changes of CO₂ up to point A1 as shown in Fig. 2. The gas phase is then converted into the liquid phase at point A2 and then goes to A3, which is at the boundary between low- and high-pressure liquids.

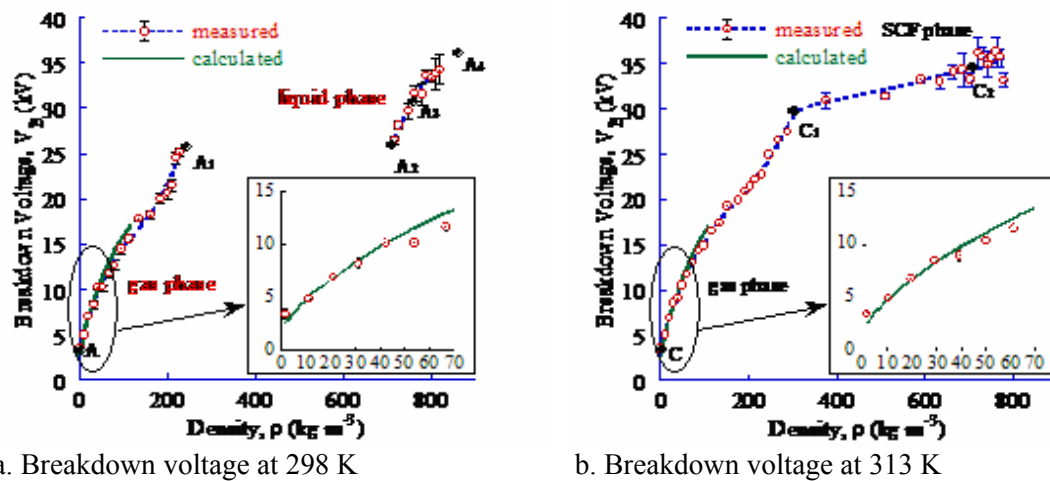


Figure 3. Breakdown voltage for plasma generation in CO₂

According to this situation, the breakdown voltage increases uniformly within this region, but in the region beyond point A3, in the high-pressure-liquid phase, the rate of increase is considerably lower than that in the low-pressure-liquid region (A2-A3). The increasing rates of breakdown voltages at 298 K are 0.08 kV/kg.m⁻³ in gas, 0.11 kV/kg.m⁻³ in the low-pressure-liquid phase, and 0.05 kV/kg.m⁻³ in the high-pressure-liquid phase. Figure 3b indicates that the rate of increase of the breakdown voltage in the gas phase is almost the same as that in Fig. 3a, but it is different in the supercritical phase (0.01 kV/kg.m⁻³) compared with the gas and liquid phases. The explanation for breakdown phenomena in the supercritical phase is still unclear; they could be related to the peculiar characteristics of supercritical fluids, such as high diffusibility, thermal conductivity, or clustering. In such conditions, the effect of bubble triggering may not be applicable to the supercritical phase.

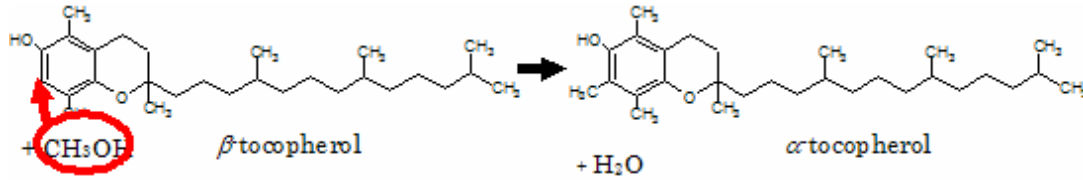
The theory of the breakdown mechanism is not well established, especially for the liquid state. However, there are two factors that may explain it: one is electronic destruction based on ionization generated by the collisions of electrons with the liquid molecules [5] and the other is cellular destruction leads to bubble triggering [6,7], which is caused by liquid evaporation due to the Joule's heat generated by current concentration at the electrode point. It is possible that bubble triggering at the tip of electrode point in the liquid phase results in complete breakdown.

3.3. Application of plasma/CO₂ to reaction of 57% tocopherol concentrate

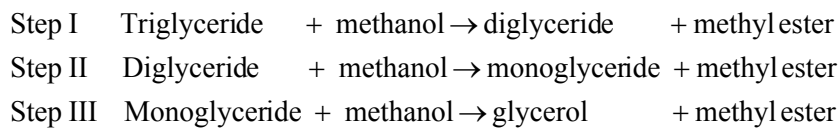
To find out what kind of reactions induced by plasma in supercritical fluid, 57% tocopherol (vitamin E) concentrate (4 mL) was mixed with methanol (20 mL) and then treated with the plasma generated in supercritical CO₂ (18 MPa, 313 K). This was done because the concentrate was extracted by

supercritical CO₂ (thus it is clearly soluble in CO₂) and contains many compounds (predominantly tocopherols, fatty acid methyl esters, sterol esters and glycerides) [8]. In this complicated system, in conjunction with methanol and catalysis, some reactions can be induced as shown by the following:

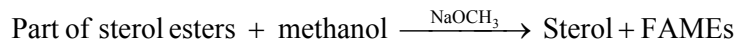
(1) Alpha conversion of other tocopherols into α -tocopherol ($T > 512$ K, $P > 8.9$ MPa with metal oxides as catalysts), for example β -tocopherol [9].



(2) Transesterification of glycerides (including tri-, di-, mono-glycerides) into FAMES (Fatty acid methyl esters) and glycerol ($T > 333$ K with NaOH or NaOCH₃ as catalysts) [10].



(3) Decomposition of sterol esters into sterols and FAMES ($T > 333$ K with NaOH or NaOCH₃ as catalysts) [11].



The experimental results show that there is an increase in the FAMES content (from 6.1% to 16.1%) compared with other compounds, indicating the possibility of decomposing glycerides into FAMES. Additionally, there is no change in the ratio of tocopherol isomers; in other words, the plasma in supercritical CO₂ cannot catalyze the alpha conversion of tocopherols.

3.4. Application of plasma/CO₂ to reaction of soybean oil

To confirm the possibility of decomposing glycerides into FAMES, we used soybean oil as the test substance, since it mainly consists of glycerides. 4 mL of soybean oil were mixed with 20 mL of methanol and the mixture was treated with the plasma generated in supercritical CO₂.

Because of the limitation of the analysis, only the volatile compounds in soybean oil could be analyzed. The analysis result showed that the main volatile compounds in soybean oil were four fatty acids, namely, palmitic acid (29.20 min), linoleic acid (32.88 min), oleic acid (32.97 min) and stearic acid (33.49 min). Additionally, their total area percentage is 75.18%.

By contrast, the plasma treatment increased the FAMES content from 3.42 to 9.23%. This result demonstrates that the plasma treatment can catalyze glycerides or fatty acids into FAMES and it can probably replace some catalysts for such reactions.

Noticeably, after each experiment there was always an obvious scar on the surface of the planar electrode. Simultaneously, some black particles appeared in the reactor and these were collected for element analysis. The analysis data show that the main elements in these particles are carbon (55.61%), hydrogen (7.87%) and nitrogen (0.78%). The same phenomena have also been observed by other researchers and these particles are considered to be carbon particles from CO₂, which was decomposed by the plasma [12].

3.5 Application of plasma/water to reaction of phenol

Phenol is one of the relatively stable compounds in near-critical water. In plasma generated in subcritical water, both hydrothermal reaction and reaction induced by plasma may occur. The experimental results showed that the decomposition of phenol was accelerated by plasma in subcritical water in comparison with reaction in subcritical water.

4. Conclusions

The breakdown voltages of electric discharges were measured in the gas, liquid, and supercritical phases of CO₂ by applying a negative DC potential at pressures in the range 0.1-14 MPa and at temperatures of 298 and 313 K in order to investigate the electric discharge characteristics. The gap between the point and planar electrodes was maintained at 200 μm. The breakdown voltage increased with an increase in the density of CO₂ in all phases, but the supercritical phase had a different rate of increase. The breakdown mechanism in the liquid phase was similar to that in the gas phase. Bubble triggering may occur in the liquid phase. The cause for the different rate of increase in the breakdown voltage in supercritical CO₂ is currently unclear.

By performing application experiments, it was found that the plasma generated in supercritical CO₂ could induce some reactions: for example, the conversion of glycerides into FAMES. However, the amount of FAMES was relatively small and the reason for this is probably that the reaction region is just limited to the gap between the two electrodes. The plasma generated in subcritical water also accelerated reaction of phenol.

Acknowledgement

This work was supported by 21st COE "Pulsed Power Science" and by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

- [1] M. A. McHugh, V. J. Krukonis, *Supercritical Fluids Extraction: Principles and practice*, Butterworths, Stoneham, MA, 1986.
- [2] T. Ito and K. Terashima, Generation of micrometer-scale discharge in supercritical fluid environment, *Appl. Phys. Lett.* 80, pp.2854-2856, 2002.
- [3] E. H. Lock, A. V. Saveliev, L. A. Kennedy, Initiation of Pulsed Corona Discharge Under Supercritical Conditions, *IEEE Trans. On Plasma Science*, Vol.33, No.2, pp.850-853, 2005.
- [4] R. Span and W. Wagner, A New Equation of State for Carbon Dioxide covering the Fluid Region from the Triple Point Temperature to 1100 K at Pressures up to 800 MPa, *J. Phys. Chem. Ref. Data*, 25, pp.1509-1596, 1996.
- [5] D. R. Young, Electric Breakdown in CO₂ from Low Pressures to the Liquid State, *J. Appl. Phys.* Vol.21, pp.222, 1950
- [6] A. H. Sharbaugh, P. K. Watson, Conduction and Breakdown in Liquid Dielectrics, *Prog. in Dielec.*, Vol.4, pp.199, 1962
- [7] K.C. Kao, Theory of High-Field Electric Conduction and Breakdown in Dielectric Liquids, *IEEE Trans. Elect. Insulation*, Vol.EI-11, pp.121, 1976
- [8] T. Fang, M. Goto, X. Wang, X. Ding, J. Geng, M. Sasaki, T. Hirose, Separation of natural tocopherols from soybean oil byproduct with supercritical carbon dioxide, *J. Supercrit. Fluids*, 2007, Vol. 40 (1): 51-58.
- [9] M. Breuninger, Preparation of α -tocopherol by catalytic methylation of other tocopherols. European Patent EP882722, 1998.
- [10] D. Swern, *Bailey's Industrial oils and fats*, John Wiley & Sons, New York, 1986.
- [11] Y. Zhao, G. Sheng, D. Wang, Pilot-Scale isolation of tocopherols and phytosterols from soybean sludge in a packed column using supercritical carbon dioxide, in *Proc. 5th Int. Symp. on Supercrit. Fluids*, Atlanta, Georgia, USA, April 8-12, 2000.
- [12] H. Kikuchi, H. Kubo, T. Tomai, K. Terashima, Deposition of Cu Film using Plasma in a Supercritical Environment, in *Proc. 8 th Int. Symp. on Supercrit. Fluids*, Kyoto, Japan, November 5-8, 2006.