Reaction in Plasma Generated in Supercritical Carbon Dioxide

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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 CO$_2$. In this study, breakdown voltages were measured in CO$_2$ in order to generate electric discharges in supercritical CO$_2$. 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 CO$_2$ 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 CO$_2$.

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
inhomogeneties 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 (CO\textsubscript{2}) 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 CO\textsubscript{2} 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 CO\textsubscript{2}. 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
CO\textsubscript{2} 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 an inspection
window 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 CO\textsubscript{2} 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 CO\textsubscript{2} 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 CO\textsubscript{2} 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 \(\mu\)m. 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 CO\textsubscript{2} medium
was in a steady state.
2.2. Application experiment using the plasma generated in supercritical CO₂
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.

2.3. GC-MS analysis

2.3.1. The tocopherol concentrate (57%)
The samples were analyzed by GC-MS (Hewlett Packard 5890 series, Palo Alto, CA, USA), coupled with a mass selective detector (HP 5972). The column used was a MS HP-5 phenyl methyl siloxane capillary (30 m × 0.25 mm i.d., film thickness of 0.25 μm). The oven temperature was increased from 353 to 488 K at 5 K/min, held at 488 K for 2 min, then raised to 548 K at 5 K/min and finally held at 548 K for 15 min. The injector temperature was 573 K, the injection volume was 1 μL, the split ratio was 20:1, the total carrier gas (helium) flow rate was 24 mL/min, and the ionizing energy was 70 eV. The main components were methyl palmitate (C16:0), methyl linoleate (C18:2), methyl oleate (C18:1), methyl stearate (C18:0), squalene, α-tocopherol, campesterol, stigmasterol and β-sitosterol. These were identified by comparing mass spectra and retention times with those of pure standards. For other components, the probability-based matching (PBM) algorithm was employed for finding the most probable match in a reference library (NIST library of mass spectra and subsets, HPG 1033A).

2.3.2. Volatile compounds in soybean oil
The temperature program was modified from that described in Section 2.3.1 in order to obtain a more reliable result. The oven temperature was increased in the sequence 413 K, 423 K, 468 K, 483 K, 513 K, 548 K at a rate of 5 K/min; the oven temperature was held constant at each temperature for 2 min with the exception of 548 K, where it was held for 22 min. The total time for this sequence was 60 min. The injector temperature was 573 K, the carrier gas (helium) flow rate was 24 mL/min, and the ionizing energy was 70 eV.

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.

Figure 2. Pressure-density diagram of CO₂

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.
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 experiment for 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 CO$_2$ (18 MPa, 313 K). This was done because the concentrate was extracted by supercritical CO$_2$ (thus it is clearly soluble in CO$_2$) 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 NaOCH$_3$ as catalysts) [10].
Step I  Triglyceride + methanol → diglyceride + methyl ester  
Step II  Diglyceride + methanol → monoglyceride + methyl ester  
Step III  Monoglyceride + methanol → glycerol + methyl ester

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

Part of sterol esters + methanol  $\xrightarrow{\text{NaOCH}_3}$  Sterol + FAMEs

The experimental results show that there is an increase in the FAMEs content (from 6.1% to 16.1%) compared with other compounds (see Fig. 4), 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.

![Figure 4. Comparison of tocopherol concentrates before and after plasma discharge](image)

3.4. Application experiment for 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 for sample 1 shown in Fig. 5 show that the main volatile compounds in
soybean oil are 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].

Figure 5. Comparison of the volatile compounds in soybean oil before and after plasma discharge

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. Consequently, in order to improve the reaction efficiency, the present batch reactor is being converted into a flow-type apparatus, which should be more stable enabling clearer results to be obtained.

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