

Wetting behavior of corn oil on stainless steel surface under dense nitrogen and carbon dioxide

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ABSTRACT

Different types of lipids and bioactive components have been isolated from complex lipid mixtures using conventional solvent extraction, and supercritical (SC) fluid extraction, and fractionation with carbon dioxide. During the fractionation process using a packed column, the surface energy of the packing material dictates the liquid interaction with the packing material. Lack of information about the role of surface energy and in turn wetting of different lipids while interacting with the packing material in the presence of supercritical fluid medium under different operating conditions was the motivation for this study. To determine the effect of pressure and temperature on this phenomenon, the interfacial tension (IFT) -(i.e. extent of wettability)- and equilibrium contact angle (CA_{eq})- (i.e. magnitude of wettability) - of corn oil in air, SC-CO₂ and N₂ on polished stainless steel (SS) metal sheet were measured at 20, 40, 60, 80 °C and 0.1, 16, 20, 24 MPa in triplicate. The IFT and CA were determined using Young-Laplace equation and height/width method, respectively. Based on the two-way analysis of variance, the CA_{eq} values under both N₂ and CO₂ were affected by temperature, pressure and their interaction at $p<0.05$. Under nitrogen environment, the CA_{eq} at 16 MPa decreased from $10.49^{\circ}\pm1.94^{\circ}$ to $4.42^{\circ}\pm1.42^{\circ}$ with an increase in temperature from 40 to 60 °C. Similarly, the CA_{eq} at 60 °C was marginally reduced from $4.42^{\circ}\pm1.42^{\circ}$ to $4.03^{\circ}\pm0.45^{\circ}$ with a pressure increase from 16 to 24 MPa. Under CO₂ environment, the CA_{eq} at 24 MPa decreased from $11.35^{\circ}\pm0.96^{\circ}$ to $7.80^{\circ}\pm0.95^{\circ}$ with an increase in temperature from 40 to 80 °C. However, the CA_{eq} at 60 °C increased from $5.41^{\circ}\pm0.41^{\circ}$ to $9.48^{\circ}\pm0.36^{\circ}$ with a pressure increase from 16 to 24 MPa. The findings indicate complete wettability of SS surface with the corn oil under both at N₂ and CO₂ media: however, the differences observed between the two systems were attributed to the mutual solubility of corn oil and CO₂, and their density differences under the experimental conditions tested.

INTRODUCTION

Various processes been developed using supercritical carbon dioxide (SC-CO₂) to separate different lipid components in high purity while avoiding the use of organic solvents. To design an optimal fractionation process, there are many variables to consider, including, the hydrodynamic behavior, which is related to the contact between the two streams and packing material. The contact of the streams involving edible oils and their by-products has been studied by different researchers. For example, Simoes et al. [1], reported two approaches to define the mass transfer models inside a packed column, considering partial and complete wettability of the packing by the dispersed liquid phase. Based on visual observations of the behaviour between diverse packings with different systems, Stockfleth and Brunner [2] concluded that the tocopherols-CO₂ mixture did not exhibit complete wettability of the Sulzer CY packing. Bejarano et al. [3] indicated the importance of contact angle (CA) and interfacial tension (IFT) to understand the hydrodynamic behavior inside a packed column. These parameters have been investigated in spray columns but not for packed columns where the limit of the interchange

area is regulated by wettability [1]. IFT has been reported for different types of lipids and surrounding phases, including corn oil [4-6]. The pendant drop method [7] has been applied most commonly to determine the IFT of lipids in supercritical fluid environment. This method employs the Young- Laplace equation:

$$\sigma_{LG} * \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2 * \sigma_{LG}}{R} - \Delta\rho * g * Z \quad (1)$$

to relate the contour of a drop at the tip of a capillary and balance the gravitational, buoyant and interfacial forces acting at the interface level of pendant drop suspended in another fluid (Fig. 1A), where σ_{LG} is the interfacial tension between the liquid and surrounding fluid, $\Delta\rho$ is the density difference between the two phases, R the radius of curvature in the apex, g is the acceleration due to gravity, Z is the distance from the apex, R_1 and R_2 are the principal radii of the drop interface at distance Z from the apex, with R_1 being the radius of curvature in the plane of Fig. 1A and R_2 the radius of curvature in a plane perpendicular to Fig. 1A.

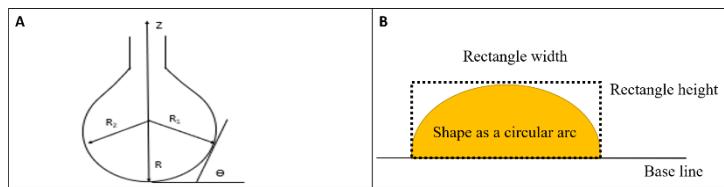


Figure 1. (A) Geometry of axisymmetric pendant drop; (B) Height/width method to determine CA.

On the other hand, when a liquid is in contact with a solid surface, molecular interactions of solid, liquid and gas phases at the three-phase contact line dictates the contact angle (CA). It can be determined by using the sessile drop method and image analysis [8]. The drop profile can be analyzed by different methods depending on the range of CA, consideration of physical phenomena and the symmetry between the right and left sides [8, 9]. For small volume drops with CA between 0° to 10°, the height/width method [10] has been used, which involves the width of the sessile drop and the height at the apex (Fig. 1B). This method considers the sessile drop phase forming a circular arc on the surface since the small drops are only slightly affected by gravity.

At atmospheric pressures and different temperatures, the CA of canola and olive oils on PTFE (polytetrafluoroethylene or Teflon) was determined under air and steam as surrounding phases [11]. In relation to high pressure conditions, several studies reported the determination of CA under CO₂ environment for different types of fluids and solid surfaces. For example, Dickson et al. [12], measured the CA of water under CO₂ environment for different glass surfaces modified with dichlorodimethylsilane (DCDMS) and silanol (SiOH). They correlated the CA with the IFT between the liquid/CO₂ with the spreading coefficient (S), which was zero when CA was 0°, indicating complete wetting [12]. However, when CA was more than zero, the S value was negative, resulting in partial wetting of the surface [12]. An increase in CO₂ pressure reflected a decrease in S because of the reduction of the liquid/CO₂ IFT [12]. Sutjiadi-Sia et al. [13] determined the CA of water-CO₂ drop phase on PTFE, glass and stainless steel (SS) with a roughness of 0.24 μm, at 0-27 MPa and 40 °C [13]. The wettability was poor, intermediate and good for the solids PTFE, SS and glass, respectively, and smaller drops could be generated when IFT was lower [13]. An important dimensionless parameter that relates the effect of gravity or surface tension over the interface of the pendant or sessile drop is the Bond number (Bo)

$$\text{Bond number} = \frac{\Delta\rho * g * R_o^2}{\sigma_{LG}} \quad (2)$$

where, $\Delta\rho$ is the density difference between the liquid and gas phase, g acceleration due to gravity, R_o the drop radius based on the volume of the pendant or sessile drop and σ_{LG} is the

interfacial tension between the liquid and gas interface. If $Bo > 1$, the gravity force dominates more than the surface force of the drop shape, showing a flattening effect on sessile drop and the pendant drop falling [14]. However, when the $Bo < 1$, the effect of gravity is neglected and drop shape approaches a sphere and pendant drop is hanging at the tip of the needle or capillary [14]. To correlate the IFT and CA with the wetting of different surfaces under CO_2 environment and evaluate the effect of pressure and temperature, several studies have been done in the oil and gas sector in relation to the enhanced oil recovery (EOR) systems. For instance, Kaveh et al. [14] evaluated the wettability of CO_2 /water/bentheimer sandstone system and related it to CA, dissolution, and bubble size of the drop [14]. The authors considered saturation and no-saturation of the surrounding medium because the dissolution of CO_2 into the drop phase affected the wetting properties [14]. They indicated that when the $Bo < 0.9$, the variation of CA became insignificant with the maximum drop diameter of 2.3 mm, providing an accurate way to evaluate the effect of pressure on the contact angle [14]. The literature lacks information regarding the wettability of metal surfaces by lipids in SC- CO_2 environment. Therefore, the objective of this study was to determine the effect of pressure and temperature on IFT and equilibrium contact angle (CA_{eq}) of corn oil in air, SC- CO_2 and N_2 on polished stainless steel (SS) metal sheet.

MATERIALS AND METHODS

Materials

Mirror-like highly corrosion-resistant 316 SS sheet (304.8 x 304.8 mm and 0.914 mm thickness) was purchased from McMaster (code: 9759K72, Aurora, OH, USA) and cut by water jet into two different dimensions (25.40 x 25.40 mm and 25.91 x 15 mm, respectively) for roughness and contact angle analysis. Acetone (HPLC grade, Fisher Scientific, Ottawa, ON, Canada), isopropanol (>98 FG purity, Sigma-Aldrich, Oakville, ON, Canada) deionized water and compressed air were used for the chemical cleaning treatment of the polished SS substrates. The drop phase was corn oil ("Mazola", ACH Food Companies, Inc., Memphis, TN, USA) that was purchased from a local market.

Apparatus to determine the IFT and CA

The system used for the determination of IFT and CA was DSA100 HP from Krüss GmbH (Hamburg, Germany), which is equipped with the High Pressure (HP) system model PD- E1700 MD (Eurotechnica GmbH, Bartelheide, Germany) and the optic system DSA100 (Krüss GmbH, Hamburg, Germany) as shown in Fig. 2. The dosing system is highlighted inside the dashed rectangle, the high-pressure system is on the right side of the schematic, the optical system is located at the bottom of the diagram, which could be used to obtain a captive bubble or to add another liquid as the surrounding phase.

IFT and CA measurements

The IFT and CA measurements were performed at 20, 40, 60, 80 °C and 0.1, 16, 20, 24 MPa in triplicate. First, the polished SS (25.91 x 15 mm) was cleaned following a protocol adopted from Beker et al. [35]. Each polished SS metal surface was cleaned with acetone, isopropanol and deionized water, in sequence. First, each metal surface was submerged into 10 ml of acetone and sonicated (model 1510, Branson Ultrasonics Corp., Sigma-Aldrich, Oakville, ON, Canada) for 2 min. Then, the same treatment was applied with isopropanol and deionized water, followed by removing the SS surface and drying for 2 min using compressed air. To ensure that the drop phase did not contain any air bubbles, several drops were formed with the HP vessel being open until no more air bubbles were seen inside the drop at the tip of the

capillary. Then the vessel was cleaned using isopropanol. The HP vessel was pre-heated to reach the targeted temperature for 45 min. The metal sheet was placed on top of the glass solid

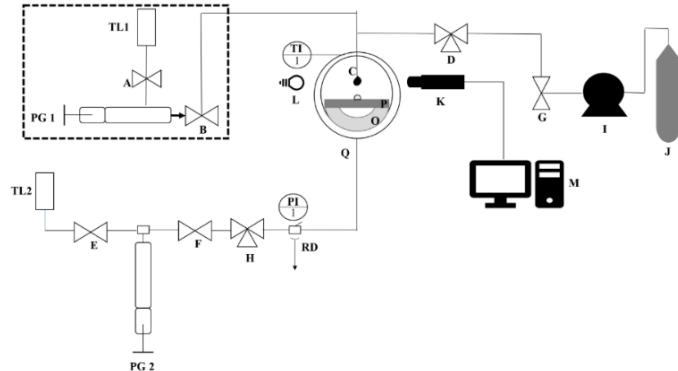


Figure 2. Schematic of DSA 100 HP system. TL1 and TL2: drop/surrounding phase liquids; A:inlet valve for liquid 1; PG1: manual piston for liquid 1; B: discharge valve of liquid valve into capillary; C:capillary (1.65 or 1.1 mm OD); D, H: drain or vent valves; PG2: hand pump; E: inlet valve for liquid 2, F: discharge valve of liquid 2; G: inlet gas valve; I: booster pump; J: CO₂ gas cylinder; K: CCD camera, L: light source; M: computer; O: glass solid substrate support; P: metal surface; Q: high pressure (HP) vessel; TI: thermocouple with temperature indicator; PI: pressure gauge.

support and introduced into the HP vessel that was closed by tightening the two sapphire windows located at each side of the vessel. To pressurize the HP vessel, valves A, B, D and H were closed, and valve G was opened slowly until the desire pressure was reached using either N₂ or CO₂. Then, valve G was closed and 5, 7 and 9 min was allowed for the system, to stabilize for target temperatures of 40, 60 and 80 °C, respectively. Then, a video was recorded at 25 and 35 frames per second for 6 min to capture all the phenomena (IFT and CA) under CO₂ and N₂ environments, respectively. To create a drop, TL1 was filled with corn oil. The valve A and PG1 were totally opened to allow the corn oil to fill the PG1. Then, valve A was closed while simultaneously PG1 was closed and valve B was slightly opened to push the corn oil into the capillary (OD=1.65 and 1.1 mm for N₂ and CO₂, respectively). Once the drop was formed, valve B was closed to avoid the detachment of the drop and 3 min were allowed to stabilize the interface of the pendant drop inside the pressurized system. Then, by slowly closing PG1 and opening valve B, the pendant drop was allowed to fall on the metal surface and converted into a sessile drop. The recording was continued for another 3 min. Later, valve D was opened slowly to depressurize the system after which, the sapphire windows, metal sheet and support were removed. A different set of three metal sheets was used at each experimental temperature. The IFT and CA were determined using Young-Laplace equation and height/width method, respectively, using pendant drop and sessile drop modules of the ADVANCE for Drop Shape Analyzers (2014-2017) software (Krüss GmbH). To get the IFT value of the pendant drop before its conversion into sessile drop, the video was converted into frames using the Free video to JPG video converter (free software). The densities of the drop phase under N₂ and CO₂ were taken from Tegetmeier et al. [15] and densities of the surrounding phase were taken from NIST [16]. All measurements at each condition were performed in triplicate and analysis of variance was performed to assess the effects of pressure and temperature as well as their interaction on the IFT and CA_{eq}, at P<0.05.

RESULTS

IFT of corn oil in N₂ and CO₂

The IFT of corn oil in N₂ and CO₂ were determined under different pressures and temperatures as shown in Table 1 and there was a substantial difference in IFT depending on the surrounding medium. The corn oil/N₂ interface displayed a moderate decrease with

increasing pressure at constant temperature. In contrast, there was a dramatic reduction in IFT of corn oil/CO₂ interface with pressure. This difference between the IFT in the two systems was due the lower solubility and diffusion of N₂ in corn oil resulting in higher interfacial tension and lower mass transfer between the phases, whereas the higher solubility, diffusion and mass transfer of CO₂ in corn oil generated a remarkable decrease in IFT. Also, at higher pressures, the temperature influence on the IFT is similar to that of CO₂ density, where the CO₂ density decreases with temperature, resulting in less CO₂ adsorption at the interface and higher IFT value [1].

Table 1. IFT and Bond number (Bo) of corn oil/N₂ and corn oil/CO₂ systems at different temperatures and pressures.

Temperature (°C)	Pressure (MPa)	IFT(mN/m) corn oil/N ₂	Bo corn oil/N ₂	IFT (mN/m) corn oil/CO ₂	Bo corn oil/CO ₂
20	0.1	33.9±0.39	0.62±0.01	33.9±0.39	0.62±0.01
40	0.1	32.0±0.32	0.62±0.01	32.0±0.32	0.62±0.01
40	16	21.9±0.40	0.65±0.001	2.5±0.14	0.61±0.04
40	20	20.0±0.42	0.71±0.006	1.9±0.14	0.64±0.02
40	24	19.3±0.47	0.64±0.01	1.8±0.08	0.56±0.06
60	0.1	24.5±0.12	0.76±0.03	24.5±0.12	0.76±0.03
60	16	21.6±0.74	0.67±0.01	4.0±0.14	0.65±0.01
60	20	20.2±0.40	0.67±0.01	2.8±0.03	0.61±0.01
60	24	18.7±0.85	0.68±0.06	2.2±0.09	0.62±0.01
80	0.1	29.9±0.95	0.63±0.01	29.9±0.95	0.63±0.01
80	16	20.9±0.74	0.66±0.04	5.9±0.3	0.63±0.01
80	20	18.5±1.23	0.74±0.06	4.7±0.25	0.63±0.01
80	24	19.6±0.19	0.67±0.01	3.7±0.25	0.60±0.05

CA_{eq} of corn oil on polished SS in no saturated N₂ and CO₂ environments

The corn oil in N₂ and CO₂ media on polished SS showed a complete wetting with values ranging from 10.49°±1.94° to 3.20°±1.15° and 11.35°±0.96 to 3.87°±0.21° for N₂ and CO₂ environment, respectively. The CA_{eq} of corn oil/N₂ and corn oil/CO₂ systems were determined over 12 s, where higher interactions between the solid, liquid and gas phases were observed, resulting in a considerable decreased in CA since drop energy was dissipating on the surface until reaching a value of zero where the CA_{eq} was obtained as shown in Fig. 3.

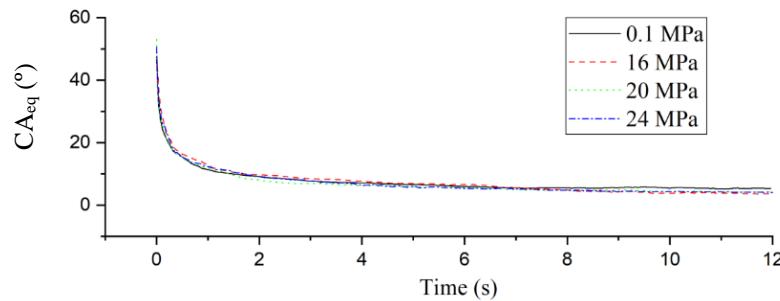


Figure 3. CA_{eq} of corn oil/N₂/polished SS system at 60 °C and 0.1, 16, 20 and 24 MPa.

Isothermal effect on CA_{eq} of corn oil/N₂ and corn oil/CO₂

The CA_{eq} of corn oil in N₂ and CO₂ environments on polished SS surface at constant temperature and different pressures (Fig. 4) revealed different behaviors because of the interaction of these gases with corn oil. Under N₂ regime, low values of CA were obtained, which could be attributed to the low mass transfer and low N₂ dissolution in the drop phase as well as the low solubilization of corn oil to the surrounding media. While under CO₂

environment, the CA_{eq} increased over the pressure range and some deposition of oil were visible which could produce a thin film of corn oil on the SS surface, creating strong interactions (autophobic phenomenon) [17,18]. These interactions resulted in higher CA values with drops bouncing before the first contact angle could be obtained at 40 °C and 60 °C. It is interesting to note that the mass transfer phenomena could influence or modify the surface energy causing the drops to bounce because of the dissolution of the drop phase in the CO_2 .

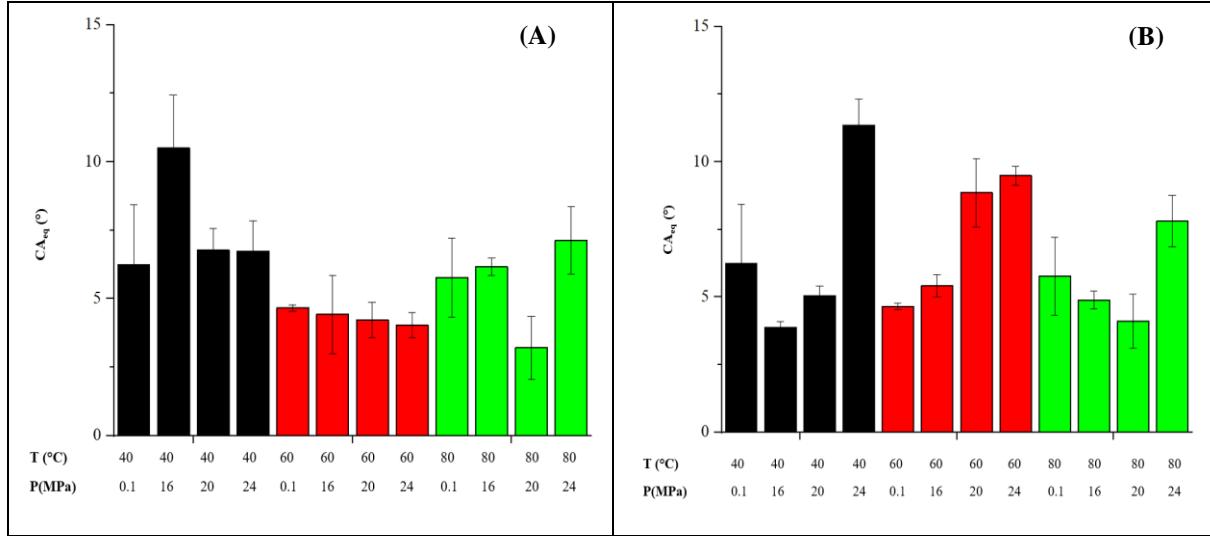


Figure 4. Isothermal effect on CA_{eq} for (A) corn oil/ N_2 and (B) corn oil/ CO_2 .

Isobaric effect on CA_{eq} of corn oil/ N_2 and corn oil/ CO_2 on polished SS

The effect of temperature under isobaric conditions on CA_{eq} of corn oil/ N_2 and corn oil/ CO_2 on polished SS is presented in Fig. 5. While corn oil/ N_2 system showed a decrease in CA_{eq} with temperature at 0.1, 16 and 20 MPa, an increase was observed at 24 MPa. This may be related to low the dissolution of N_2 that resulted in higher IFT values or volatilization effect. In contrast, corn oil/ CO_2 showed a decrease in CA_{eq} at 24 MPa when the temperature was increased. It can be attributed to the higher solubility of corn oil in CO_2 at this pressure, which allowed extraction of some light components of the drop phase into the surrounding phase and then, the wetting of the corn oil on the SS surface was affected, resulting in higher values in comparison with 0.1, 16 to those obtained at and 20 MPa.

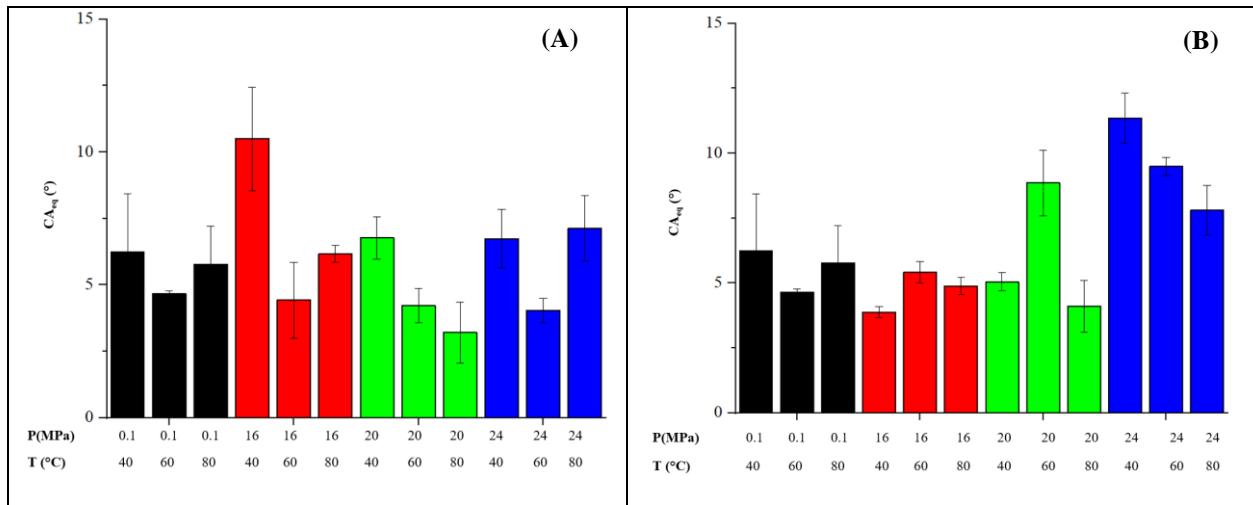


Figure 5. (A) Isobaric effect on CA_{eq} for corn oil/ N_2 and **(B)** corn oil/ CO_2 .

CONCLUSION

The wetting behavior of corn oil on polished SS surface under dense N₂ and CO₂ was characterized as complete wetting, but there were significant effects of pressure and temperature on the equilibrium contact angle (CA_{eq}). Gas dissolution into the drop phase, extraction of light components, the density differences between the phases, the IFT values of the drop phase, autophobic behavior of the metal sheet and bouncing of drops on complete wettable substrates were some of the phenomena observed under CO₂ environment in contrast with the N₂ environment. A detailed analysis of these no peculiar observations is ongoing task.

ACKNOWLEDGEMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada for their financial support and Dr. Philip Jaeger and Eng. Ryan Baily for their assistance during this study.

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