

Recovery of carboxylic acids from dilute aqueous solutions using a supercritical CO₂ packed column

A. Novella^{a,*}, N. Gañán^b, S. Camy^a, J.-S. Condoret^a

^aUniversité de Toulouse, INP, UPS, Laboratoire de Génie Chimique UMR CNRS 5503, 4, Allée Emile Monso, F-31030 Toulouse, France

^bInstituto de Investigación y Desarrollo en Ingeniería de Procesos y Química Aplicada, Universidad Nacional de Córdoba, Argentina

* astrid.novella@ensiacet.fr

ABSTRACT

In the present work, the recovery of acetic acid from diluted aqueous solution using high pressure CO₂ is considered. The aim of this study is to evaluate the performance of a counter current extraction process for this system in a simple configuration using a 2m height and 17mm diameter column, packed with 3mm Dixon rings. Experimental results are compared to simulations using a rate-based model. Theoretically, operating at 40°C and 10 MPa, for a 0.5 kg/h feed at 5% acetic acid mass fraction, we obtained a 44% acetic acid mass fraction in the extract, with a recovery ratio equal to 30%, when a solvent-to-feed ratio of 10 was used. The thermodynamics behaviour of the ternary system was described with the GC-PPC-SAFT equation of state, and embedded in the simulation program, whose results proved to agree with the experiments.

INTRODUCTION

Recovery and purification of products from fermentation broth is an important issue because of emergence of biorefineries for synthesis of added-value products, biofuel, pharmaceuticals molecules or chemical building blocks, as for instance carboxylic acids. Feedstock cost, in one hand, and downstream processing, on the other hand, dominate the biological production cost of carboxylic acids [1]. Carboxylic acids can be produced from renewable raw materials by fermentation and used in many applications on large scale. Some of them, like succinic acid, levulinic acid or 3-hydroxypropionic acid belong to the top chemical opportunities from carbohydrates mentioned in the top 10 list of biobased chemicals by the U.S. Department of Energy in 2004 [2]. In the present study, as a model system, the water-acetic acid mixture was chosen because thermodynamics was already described in the literature [3][4], which is not the case for water-succinic acid mixtures for example. Acetic acid, as well as levulinic acid, exhibit a non-negligible solubility in pure scCO₂, which is unusual for carboxylic acids [5]. Acetic acid is the most widely used aliphatic carbonic acid. Biobased acetic acid represents only 10% of global market of this acid [6]. One way of production of acetic acid and other interest carboxylic acids is represented in Fig. 1.

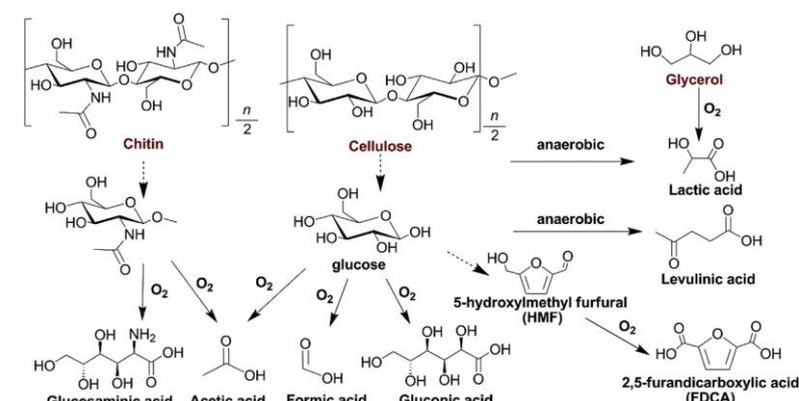


Figure 1. Biomass conversion in acetic acid and others carboxylic acids [7]

High production yield of acetic acid can be obtained and conventional purification is done either by distillation, inducing high energy consumption because of close volatility of compounds, or reactive extraction with di-2,4,4-triméthylpentyl-n-octyl phosphine oxide or tri-2,4,4-diméthylpentyl phosphine oxide [8]. Nowadays, other separation methods such as extractive distillation or hybrid extraction/distillation processes are investigated but addition of separation agents is needed (isobutyl acetate, isopropyl acetate, etc.) [9]. Such drawbacks can be alleviated by the use of supercritical CO₂ as it was proposed for fractionation of alcohol-water mixtures [10]. Such a process for purification of organic acid-water solutions has been rarely addressed because the rather low solubility of these acids in pure scCO₂ does not encourage to test such a process. Only a few studies have considered the recovery of acetic acid, in a batch mode or semi-continuous mode [11][12].

MATERIALS AND METHODS

Materials

Carbon dioxide was supplied by Air Liquide (\geq purity 99.98%) and acetic acid is from Sigma-Aldrich (\geq purity 99.5%).

Experimental set-up

The experimental set up (Fig. 2a) consists of a 2m high column with 17 mm internal diameter, filled with random Dixon packing (Fig. 2b) which are cylinders made of metallic mesh gauze with the following geometrical characteristics : 3 mm (1/8") length and diameter, specific area of 2378 m²/m³ and void fraction ϵ of 0.91. The high pressure column is thermally insulated and equipped with four temperature sensors equally distributed all along the column height. A specific device made of two automatic valves in series, alternatively closed and opened by a timer placed at the bottom of the column is used to recover the raffinate in a pseudo-continuous mode. At the top of the column, two separators in series allow recovering the liquid extract free of CO₂ thanks to decompression. The extraction procedure was as follows: the output liquid from the CO₂ bottle is subcooled in a heat exchanger up to 5°C and then pumped using a high pressure positive displacement diaphragm pump with a maximum capacity of 7 kg/h. The pressurized liquid CO₂ is then heated to the desired temperature for the extraction. The CO₂ is fed at the bottom of the column and flows upward counter-currently with the downward dilute aqueous solution of acetic acid (5% w/w) feed. The liquid feed is pre-heated to the chosen temperature and introduced at the top of the column using a high pressure membrane pump with a maximum capacity of 2.4 kg/h. The column is operated in the trickle bed mode, supercritical CO₂ being the continuous phase. Operating conditions at the raffinate separator were 20°C and atmospheric pressure. The extract was recovered at 6 MPa and 25°C in the first separator and 0.1 MPa and around 0°C in the second one. Analysis of the compositions of the different liquid phases was simultaneously performed by UV-visible spectroscopy technique and refractometry.

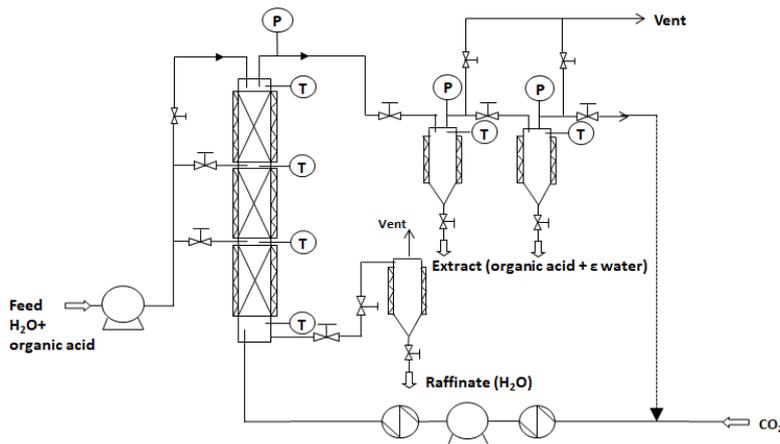
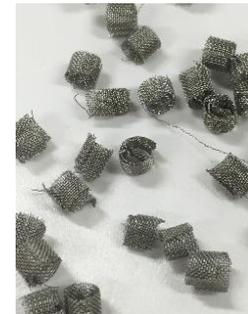


Figure 2. (a) Experimental set-up



(b) DIXON packing

MODELLING

Phase equilibria of the acetic acid-water-CO₂ ternary system

Knowledge of phase equilibria of the ternary system is crucial to understand the process of extraction. In view of process simulation, a thermodynamic model must be chosen and validated by comparison with equilibrium experimental data. The most widely used thermodynamic models for mixtures at high pressure with CO₂ are cubic equations of state. However, important characteristics of acetic acid-water-CO₂ system are polarity and possible creation of hydrogen bonds or other strong bonds (intermolecular interactions). Recent thermodynamic models, such as SAFT (Statistical Associating Fluid Theory) and derivatives of SAFT, can take into account these intermolecular interactions and high polarity. One of these models, GC-PPC-SAFT (Group Contribution Polar Perturbed Chain Statistical Fluid Theory) was used here to predict the ternary mixture behaviour. This model is based on the Wertheim theory or perturbation theory. General expression of SAFT equation describes residual Helmholtz free energy as the addition of different terms like dispersion term, associative term or chain formation term:

$$A^{res} = A^{hc} + A^{disp} + A^{chain} + A^{assoc} + A^{multi-polar} \quad (1)$$

Molecules are described with possible associative sites with letter from A to D (A means all sites have a zero charge, B means the first site has a positive charge and the other negative charges, etc.). Carboxylic acids may have two possibilities, 1A and 2B, water four possibilities 2B, 3B, 3B and 4C, and carbon dioxide is non-associating. Formally, water has two similar acceptor sites and each hydrogen a donor site therefore water should be 4C (Fig. 3) and indeed it is the most used description in the literature [13].

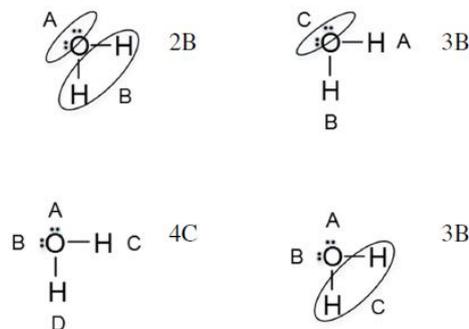


Figure 3. Possible associative sites for water

Acetic acid is a small chain acid with a particular behaviour because of hydrogen bond formation between two carboxylic groups of two molecules leading to formation of cyclic dimer molecules in the vapour phase (Fig. 4). Therefore, 1A model is used for acetic acid because it often offers the best predictions [14].

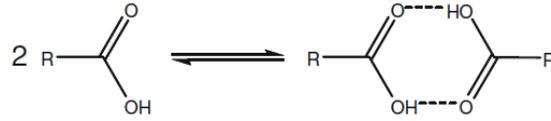


Figure 4. Carboxylic acids dimerisation [14]

Phase equilibrium data are available in the literature for the ternary system [3][4]. The model gives good predictions for each binary sub-systems and for the ternary system too. Temperature dependant binary interaction coefficient are established according to experimental data for GC-PPC-SAFT. Average Absolute Relative Error (AARE) conferring to following equation (Eq. 2), are indicated in table 1 for binary sub-systems and table 2 for ternary system.

$$AARE_{zi} = \frac{100}{Np} \sum_{i=1}^{Np} \left| \frac{z_i^{exp} - z_i^{calc}}{z_i^{exp}} \right| \quad (2)$$

Table 1 : AARE (%) for binary sub-systems

i	j	Range	Np	AARE _{x_i} (%)	AARE _{x_j} (%)	AARE _{y_i} (%)	AARE _{y_j} (%)
CO ₂	AA	[313.2-353.2] K [1.1-11.1] MPa	25	0.72	0.63	0.77	45.01
CO ₂	H ₂ O	[323.15-353.1] K [4.05-17.8] MPa	36	2.07	0.03	0.04	8.05
AA	H ₂ O	[296-445] K [0.003-0.791] MPa	34	18.42	8.27	20.56	13.17

Table 2 : AARE (%) for ternary system

Ternary system	Np	AARE _{x_{CO2}} (%)	AARE _{x_{AA}} (%)	AARE _{x_{H2O}} (%)	AARE _{y_{CO2}} (%)	AARE _{y_{AA}} (%)	AARE _{y_{H2O}} (%)
AA-H ₂ O-CO ₂	78	12.87	2.64	3.31	1.14	32.91	19.70

Type I or type II ternary diagram are obtained according to different operating conditions (Fig. 5). Type I diagram is a better configuration for simple extraction but knowledge of thermodynamic behaviour for each condition is important, especially when considering a possible implementation of internal reflux, where Type II system can be exploited [15].

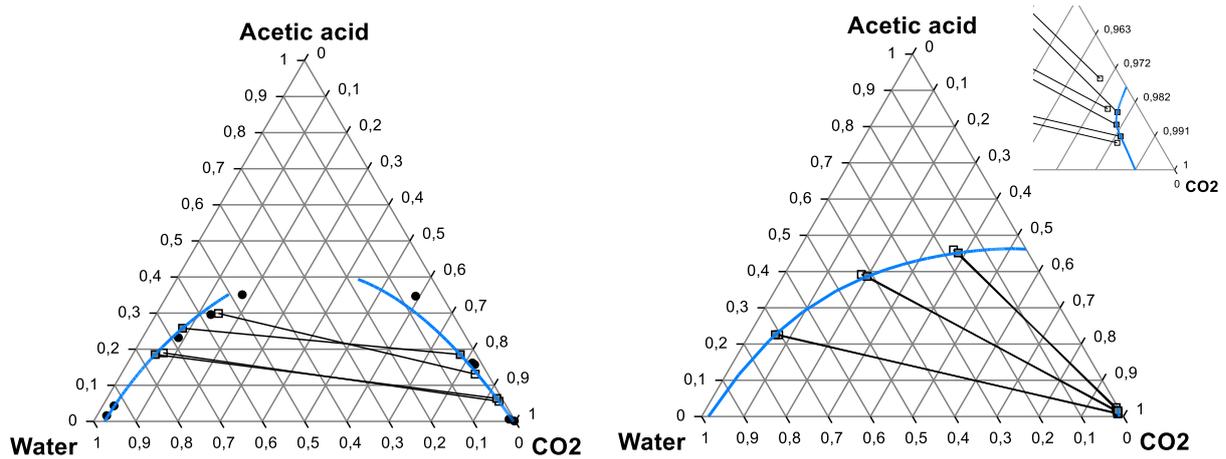


Figure 5. Left: Type I ternary diagram for acetic acid-water-CO₂ system for 40°C and 10 MPa & Right: Type II ternary diagram for acetic acid-water-CO₂ system for 80°C and 10 MPa. (--) equilibrium line calculated, ■ calculated points, ● experimental data from Panagiotopoulos [3], □ experimental data from Bamberger [4]

Modelling of the supercritical extraction column

Two different approaches can be used for modelling a supercritical extraction column: a method based on the equilibrium stage concept and a non-equilibrium method also called rate-based method. The equilibrium stage method was mostly proposed [16] but in our previous works about recovery of isopropanol [17] it proved to be unsatisfactory.. Therefore a rate-based method was investigated in this work. This approach, used for example by Martín [18], allows to compute the mass transfer resistance of the two phases, yielding to a better understanding of the coupling of physical and thermodynamic phenomena. The model was implemented in the Matlab[®] software by N. Gañán [19] where all details are given. Briefly, it can be described as a set of differential mass balance equations for all the components i in each phase (supercritical phase F and liquid phase L) accounting for local mass transfer and assuming phase equilibrium at the interface. The mass transfer coefficients are calculated according to Onda like equations 3 and 4:

$$k_{F,i} = \alpha \left[(a_p d_p)^{-2} Re_F^{0.7} Sc_F^{0.33} \left(\frac{D_{i3}}{d_p} \right) \right] \quad (3)$$

$$k_{L,i} = \beta \left[(a_p d_p)^{0.4} Re_L^{0.66} Sc_L^{-0.5} \left(\frac{\mu_L g}{\rho_L} \right)^{0.33} \right] \quad (4)$$

This model was previously validated thanks to experimental data about supercritical fractionation of isopropanol solutions [17] where α and β are parameters to adapt Onda's correlations (Eq 3 and 4) to high pressure system. From experimental results in [17] α and β were identified, respectively equal to 5.23 and 0.0051.

RESULTS

Although acetic acid compositions in raffinate and extract were both analysed, only results concerning raffinate composition have been considered to be relevant, because for the extract, imperfect recovery and small quantities recovered resulted in too high uncertainties. Therefore the results are presented in terms of acetic acid recovery and content in the raffinate. For a better understanding of results, an enrichment factor is defined and calculated as the ratio of the mass fraction of acetic acid from CO₂-free extract to the mass fraction of acetic acid in the feed.

Fig. 6 shows the influence of solvent-to-feed ratio (S/F) at 10 MPa and 40°C with a 5% w/w acetic acid feed at 0.5 kg/h. For the all tested CO₂ flow rates values, no flooding was detected in the column.

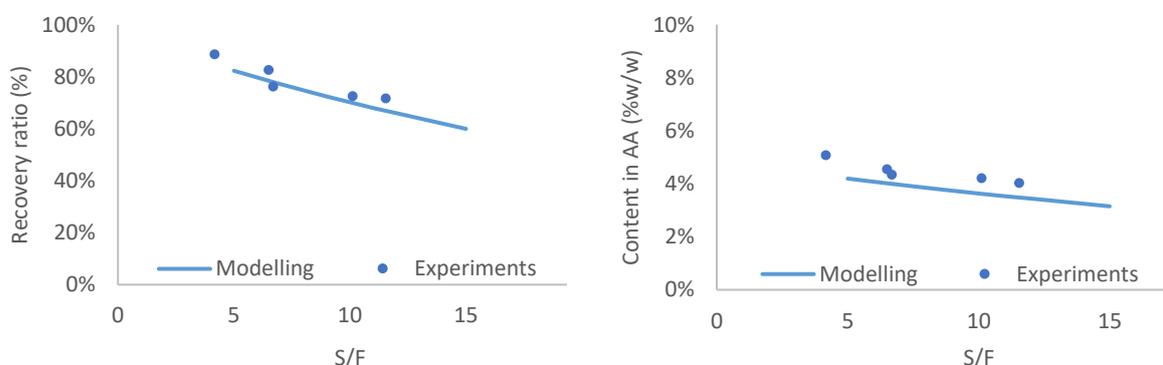


Figure 6. Influence of S/F on the recovery ratio of AA and content of AA in the raffinate (10 MPa, 40°C, F=0.5 kg/h, 5% w/w AA)

According to experimental results, increasing solvent-to-feed ratio (from 4 to 11) leads to a decrease of the recovery ratio of acetic acid in the raffinate from 89% to 72%. Content of acetic acid in the raffinate also decreases of about 1%. It can be seen from Fig. 6 that modelling overvalues fractionation performance in terms of recovery and purity of the solute in the raffinate and, consequently, in the extract but the experimental trend is respected. Concerning the extract, modelling predicts a decrease of content in AA from 48% to 42% because of co-extraction of water but the recovery of AA is double (40%) from S/F=5 to S/F=15. Therefore, a S/F of 10 (according to experimental convenience) was chosen for the other runs.

The influence of pressure (Fig. 7) was experimentally evaluated at 10 and 15 MPa at 40°C, S/F=10 and with 5% w/w acetic acid feed at 0.5 kg/h. Increasing the pressure resulted in a decrease of raffinate acetic acid recovery and acetic acid content, due to the expected increase of the CO₂ solvent power.

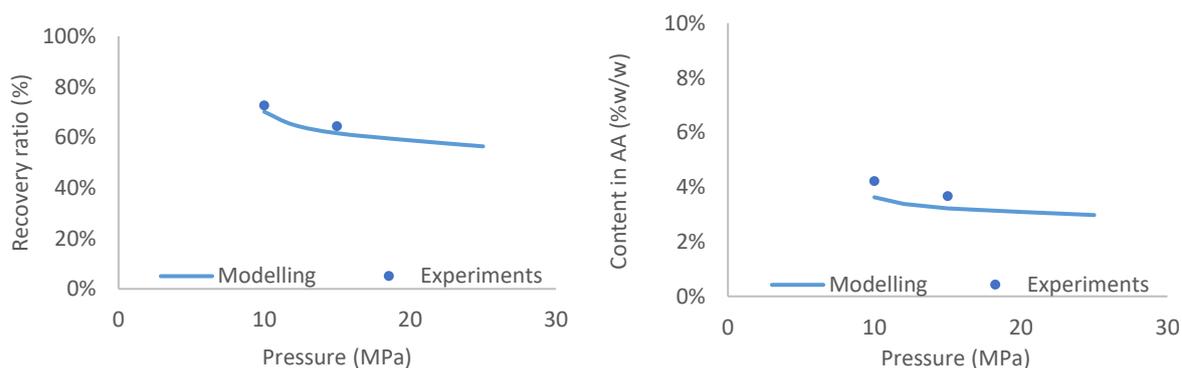


Figure 7. Influence of pressure on the recovery ratio and content of AA in the raffinate (40°C, S/F=10, F=0.5 kg/h, 5% w/w AA)

Fig. 7 shows that modelling and experiments are in agreement with a slight tendency of the modelling, here again, to overvalue purification performances. Experimentally, at 15 MPa, 3.7% of acetic acid is contained in the raffinate with a recovery ratio of 64%. According to modelling, at 15 MPa purity of AA in the extract is equal to 44% with recovery ratio of 38%. When pressure increases from 15 to 25 MPa, modelling predicts a decrease of the acetic acid content in the raffinate from 3.22% to 2.97% and a decrease of the acetic acid recovery ratio in

the raffinate from 62% to 56% but water recovery ratio in the raffinate also decreases from 97% to 96%, indicating the co-extraction of water. When pressure is increased, the computed enrichment factor slightly decreases (8.9 at 10 MPa and 8.4 at 25 MPa) because of increased co-extraction of water. Nevertheless, computed recovery ratio of acetic acid in the extract increases from 30% to 44%. From a point of view of the extract, increasing the pressure improves the extraction of AA but selectivity is lowered.

Finally, the influence of the temperature has been studied in the range of 40-80°C for a pressure of 10 MPa, S/F=10 and 5% w/w acetic acid in the feed (0.5 kg/h) and results are presented in Fig. 8.

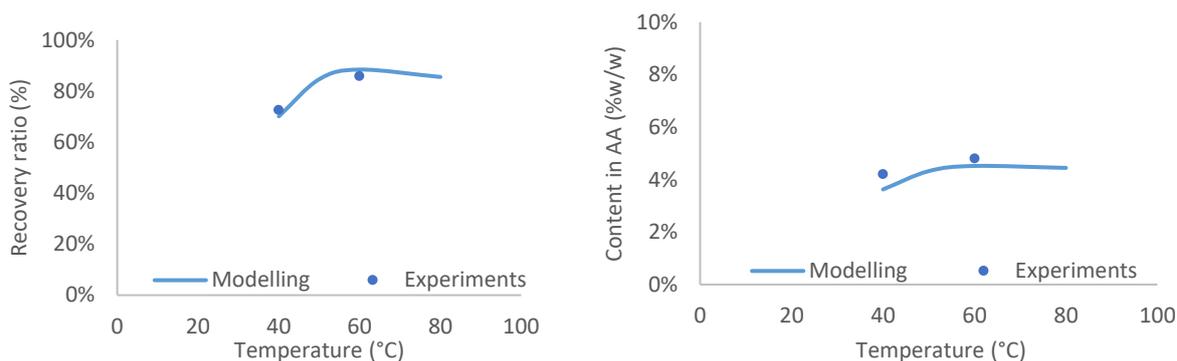


Figure 8. Influence of temperature on the recovery ratio and content of AA in the raffinate (10MPa, S/F=10, F=0.5 kg/h, 5% w/w AA)

In this case too, modelling is in good agreement with experiments at 40 and 60°C. Experimentally, when temperature is increased from 40°C to 60°C, raffinate is more concentrated in acetic acid (4.2% to 4.8%) and recovery ratio in acetic acid in raffinate also increases (73% to 86%) which means that extraction is not favoured by temperature at this condition of pressure. Consequently, the enrichment factor considerably decreases when temperature increases (from 6 to 2) and recovery ratio in the extract is divided by two. At 10 MPa, a lower temperature is thus a better choice for supercritical extraction of acetic acid as confirmed by modelling results (44% of AA in the extract at 40°C against 26% at 60°C).

CONCLUSION

Feasibility of supercritical purification of carboxylic acids solutions has been considered through the study of recovery of acetic acid using a scCO₂ packed column operated in the continuous mode. The influence of operating conditions was evaluated by modelling and compared to our first experimental results. In a simple configuration (without internal or external reflux), a computed enrichment factor of 9.6 could be obtained in the extract free of CO₂ at a pressure of 10 MPa, a temperature of 40°C and a solvent-to-feed ratio of 5. Enrichment factor and recovery ratio of the solute in the extract are the two main objectives in the choice of operating conditions. It was also shown that a low temperature is favourable, as expected according to thermodynamic study.

Solvent-to-feed ratio and pressure have to be chosen as a function of purity in the extract and recovery ratio in the extract. With the configuration of our experimental set up, as expected, quite low degree of recovery was obtained due to moderate solubility of AA in CO₂ and low selectivity of CO₂. Future experiments and modelling with implementation of a temperature induced reflux could be an option for increasing separation performance.

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