Biodiesel from Soybean Oil Transesterification Assisted by Ultrasonic Irradiation

José M. Encinar, Gloria Martínez, Juan F. González, Nuria Sánchez, and Dolores Álvarez

***Abstract*—Biodiesel has been produced by transesterification of soybean oil by methanol. This reaction, heterogeneous, only takes place in the interphase alcohol triglyceride. Low-frequency ultrasonic irradiation produces an emulsion of the two immiscible liquids, improving mass transfer and getting that the chemical reaction controls the kinetic of the process. This causes an increase of the reaction rate, decreasing time of reaction.**

Abatch and a continuous process were carried out, using potassium hydroxide as catalyst. A Branson processor of 20 kHz was used in all of the experiments. In the batch process methanol: oil molar ratio (3:1 to 15:1), maximum temperature (70 and 100 ℃) and ultrasound amplitude (40 to 100%) were studied. In the continuous process, methanol: oil molar ratio (6:1, 12:1 and 15:1) and catalyst concentration (0.28 to 0.70 g.mL^{-1}) were evaluated. In the first process, MeOH:oil molar ratio influenced on the yield, while temperature did not exercise influence. Amplitude affected reaction rate, but the conversion achieved was similar after 15 minutes. In the continuous process, the MeOH:oil molar ratio influenced in the reaction, while the concentration of catalyst had a positive effect only to low residence times.

***Index Terms*—Biodiesel, soybean oil, transesterification, ultrasonic irradiation.**

I. Introduction

The biodiesel is a renewable fuel, biodegradable, nontoxic, easy to produce and manufactured with raw materials of agricultural origin [1], [2]. For these motives, this product is an attractive alternative to the mineral diesel oil. The biodiesel consists of a mix of methyl-esters of long chain fatty acids. Vegetable oils, as soybean oil, or animal fats, are suitable raw materials to obtain this fuel [3]. The triglycerides, which compound vegetable oil, were turned in esters by transesterification. In this reaction, triglycerides react with an alcohol of short chain, methanol habitually, in order to produce esters and glycerol. The process should be carried out in the presence of a catalyst in order to achieve a suitable reaction rate. Catalysts more used are strong bases such as hydroxides or methoxides of potassium and sodium [4].

The transesterification reaction is initially a heterogeneous system and relatively slow, since alcohol and oil phases are not miscible. Hence, initially the reaction only takes place in the interphase alcohol-oil and the process is controlled by mass transfer. Ultrasonic energy is known to produce unique chemical and physical effects because of the growth and the collapse of cavitations bubbles. A low frequency ultrasonic irradiation can be used to produce emulsions from immiscible liquids and, in consequence, it can benefit chemical reactions such as the transesterification [5]-[7]. In the chemical processing, ultrasound enhances both mass transfer and chemical reactions, offering potential for shorter reaction times, cheaper reagents and less extreme physical conditions [8]. Lower rates of synthesis have been typically attributed to mass transfer limitations due to heterogeneous conditions, existing during the reaction. The use of cavitational reactors can favor the chemical reaction and propagation, leading to the enhanced mass transfer and interphase mixing. Therefore, the required operating conditions are usually less severe, in terms of temperature and pressure [9].

The objective of this work is the application of ultrasonic irradiation to assist the basic transesterification reaction of soybean oil with methanol. The variables affecting the methyl ester yield during the transesterification reaction, such as, amount of catalyst, methanol: oil molar ratio and ultrasonic power and frequency were investigated to optimize the reaction conditions. Also, the way to carry out the process, if it was continuous or batch processing, was also researched.

II. Materials and Methods

The soybean oil was provided by the Research Center "La Orden-Valdesequera" (Badajoz, Spain), Section of Non-Food Crops. Potassium hydroxide (KOH) was supplied by Merck (pellets GR for analysis), methanol (MeOH), 96%, was purchased from Panreac. All other chemicals were obtained commercially of analytical grade.

Methyl ester content was assayed by gas chromatography in a VARIAN 3900 chromatograph, provided with a FID, employing a silica capillary column of 30 m length, 0.32 mm ID, and 0.25 mm film thickness. Heptane was used as solvent, and the carrier gas was helium at a flow rate of 0.7 mL min-1. The injector temperature was kept at 270 ℃, and the detector temperature, 300 ℃. Temperature ramp started with 200 ℃, and then went 20 ℃/min up to 220 ℃. Calibration curves for all of the ester analyzed were carried out as in previous works [10], [11], obtaining linear plots.

As has been indicated, the transesterification of soybean oil was carried out by batch and continuous processing. In both, a digital processor Branson of 20 kHz, with adjustable amplitude from 10 to 100 % and maximum power of 400 W was used. In batch process a spherical glass reactor of 500

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mL was used. A thermometric probe connected with digital processor controlled the temperature of the reaction. The reactor was supplied with a condensation system and a sampling system, to follow the progress of the reaction. In continuous process, the jacketed reactor of 36 mL of capacity was made of stainless steel, and it was supplied with a refrigeration system. The temperature of the fluid at the outlet of the reactor was determined by a thermometric probe. Fig. 1a and 1b show the experimental installations.

In the discontinuous process, the reactor was charged with fixed amounts of oil, MeOH and KOH for each reaction. Amplitude, maximum temperature and reaction time (15 min) were programmed. The ultrasonic processor was switched on at reaction time equals zero. Then the progress of the reaction was followed by the analysis of periodic samples. Samples were cooled to stop the reaction and they were washed to remove glycerol, catalyst and the excess of methanol. Remaining water was removed by heating at 110 ℃. The cleaned samples were analyzed by gaseous chromatography, in order to determine their ester content.

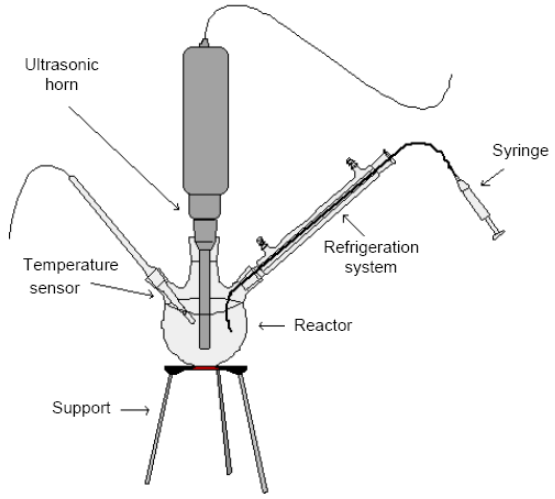


Fig. 1. (a). Experimental setup. Batch process. (b). Experimental setup. Continuous process.

In the continuous process, peristaltic pumps were used to feed the reactor from the bottom at an established flow. There were two pumps, one of them flushed the oil and the other one a mixture of catalyst and alcohol with the desired concentration for each reaction. Before starting the reaction, the reactor was charged with the established amounts of reagents. Then the amplitude was programmed and the ultrasonic system was activated. The process was kept up to the reaction reached stationary regime. To check the state of the reaction, some samples were taken. Then they were washed and analyzed as it was mentioned before.

III. Results and Discussion

A. Batch Process

Generally, the most influential variables in a transesterification reaction are catalyst concentration, MeOH:oil molar ratio and reaction temperature [4].

In this work catalyst concentration was kept as a constant factor, with a value of 0.5 wt % of KOH, because it is considered a suitable catalyst concentration to achieve the progress of the reaction in short time. In addition, this variable had slight effect on previous works where transesterification reaction was assisted by ultrasonic irradiation [10].

The molar ratio of methanol to oil was considered worthy to study its effect on ultrasonic-assisted transesterification. In order to get this aim, the rest of variables were kept at a constant value, such as 70 ℃ and 60 % of amplitude (this value is the maximum amplitude allowed by the equipment under these conditions).

The MeOH:oil molar ratio was varied from 3:1 to 15:1 and the results were plotted in Fig. 2. In this graph was collected the methyl ester content of the biodiesel and the reached temperature depending on the reaction time for experiments with different MeOH: oil molar ratio. To make easier the analysis of the data, in Fig. 3 were shown the projection planes of the data drawn in Fig. 2.

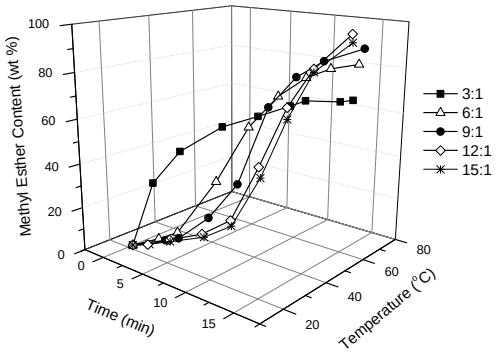
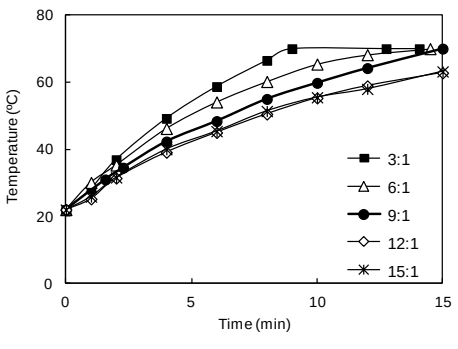
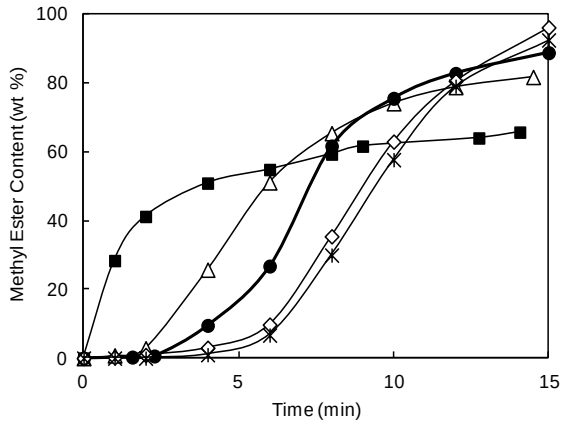


Fig. 2. Methyl ester content and temperature depending on the reaction time for reactions with different MeOH:oil molar ratio.



(a)



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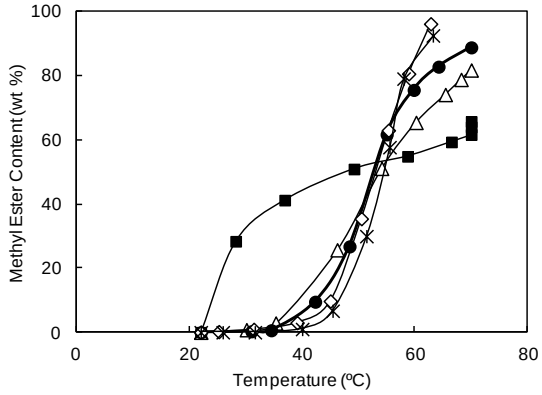


(c)

Fig. 3. Planes of tri-dimensional graph shown in Fig. 2.

The evolution of reaction temperature along the reaction time was showed in Fig 3a. It can be seen that ultrasonic energy increases the temperature of the medium,therefore the transesterification reaction was developed in non isothermal process.

The higher MeOH:oil molar ration, the slower increase of the medium temperature. This fact was observed because there was higher reagent amount when methanol percentage was bigger. Hence, the methyl ester content will depend on the MeOH:oil ratio, as well as, the reaction temperature.

As shown in Fig. 3b, the transesterification reaction will be faster when MeOH:oil molar ratio is lower, although the ester content reached at the equilibrium will be higher when higher amount of MeOH was used. The initial speed of the reaction is related with the contact between reagents[12]and the less methanol, the higher temperature and agitation, so when few amount of methanol is fed to the reactor, ultrasound will manage stronger mixture of reagents. Then, the reaction will be developed with higher speed initially.

On the other hand, in Fig. 3b and Fig. 3c there is an induction period for all reaction except the one with 3:1 molar ratio. This fact could be explained because the less amount of MeOH, the easier mixture of the components is.

As it was previously seen, the reactions were carried out in non isothermal way. The ultrasonic processor allows maximum temperature was fixed, so that two reactions with different maximum temperature were realized to check whether this parameter affects the temperature of the medium or the methyl ester content.

In Fig. 4 it can be seen that both reactions followed the same temperature profile and the evolution of methyl ester content was the same along the time. Hence if maximum temperature is higher than reaction temperature, this parameter will not influence in the progress of the reaction; it will act as a safety measure.

The amplitude of the ultrasonic processor means the power of the ultrasonic irradiation which is applied by the equipment. Several reactions were carried out with different amplitude of ultrasound, using 12:1 as MeOH:oil molar ratio and 70 ℃ as maximum temperature allowed. The results were showed in Fig. 5 and Fig. 6.

As can be seen in Fig. 5 and also in Fig. 6a, 6b and 6c, when the ultrasonic power was increased, the temperature increased, too. Thus the more power was applied, the more agitation of the medium was managed. Both facts benefited the reaction between triglycerides and methanol and a higher speed was achieved when the amplitude was increased.

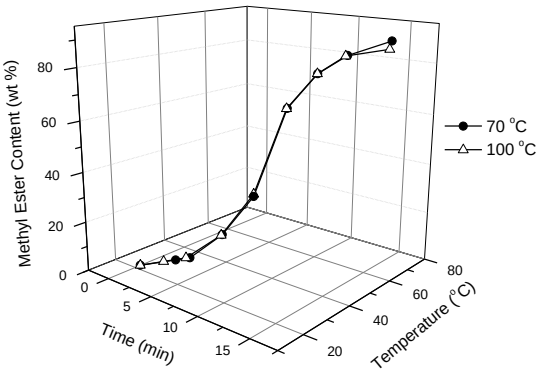


Fig. 4. Methyl ester content and temperature depending on the reaction time for reactions with different programmed maximum temperature.

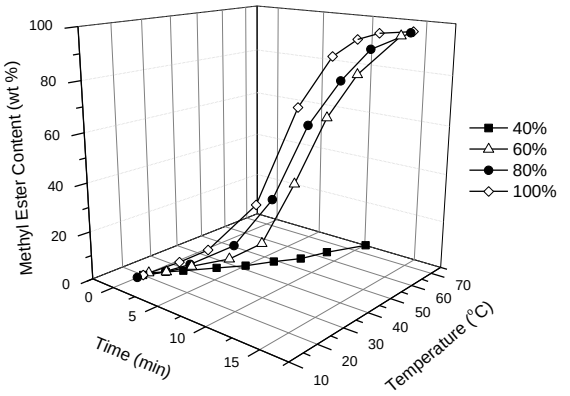


Fig. 5. Methyl ester content and temperature depending on the reaction time for reactions with different amplitude of ultrasonic radiation.

Chemical equilibrium was reached with all amplitudes except 40 % and the ester content in the equilibrium was the same in all reactions. In consequence, the reaction speed must be balanced against the energy cost to establish the most suitable amplitude for the system.

B. Continuous Process

In the continuous process, the application or no application of cooling, the MeOH:oil molar ratio and the catalyst concentration were studied. These variables represent the ratio between reagents and catalyst, besides the reaction temperature, which are the most influential variables in the transesterification reaction [4]. The reactor used in this part of the work is a new reactor, so there is not previous references which can show the expected behavior

when these variables are changed.

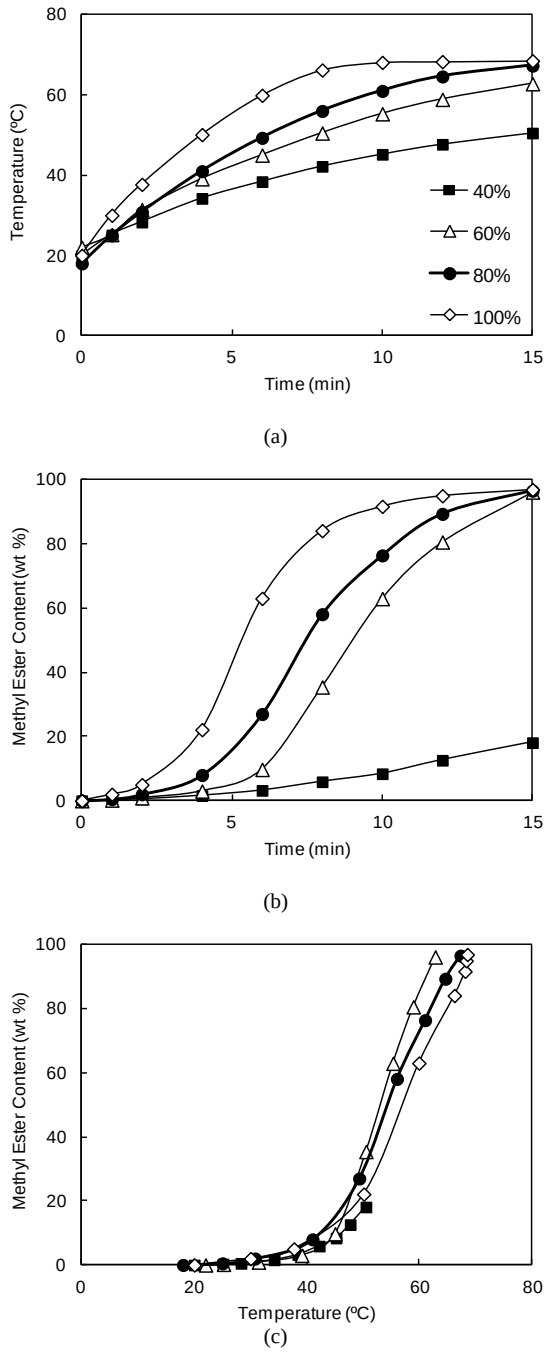


Fig. 6. Planes of tri-dimensional graph shown in Fig. 5.

Firstly some previous runs were carried out by continuous processing. It was observed that 75 ℃ were reached as medium temperature after 7 min of reaction, therefore refrigeration was applied by a flow of cool water through the jacket of the reactor.

The experiments were performed with a catalyst concentration of 0.0035 g mL^{-1} and 100 % of amplitude. MeOH:oil molar ratio was varied, 6:1 and 12:1 were used. And several residence times were checked between 1 and 7 min. The results of this set of reactions were plotted in Fig. 7a, 7b and 7c.

As can be seen in Fig. 7a, the medium temperature was strongly softened when refrigeration was used. In addition, medium temperature was lower when MeOH:oil molar ratiowas 12:1 instead of 6:1. Higher MeOH:oil ratio also led to higher ester content in the biodiesel, as was shown in Fig. 7b. Considering the reaction with and without refrigeration system, when water of refrigeration was used higher ester contents were achieved at higher residence time. However, without refrigeration system the ester content decreased when residence time increased. A possible explanation for this behavior is that the medium temperature was higher than methanol boiling point, 64.5 ℃, therefore leaks of methanol could happen.

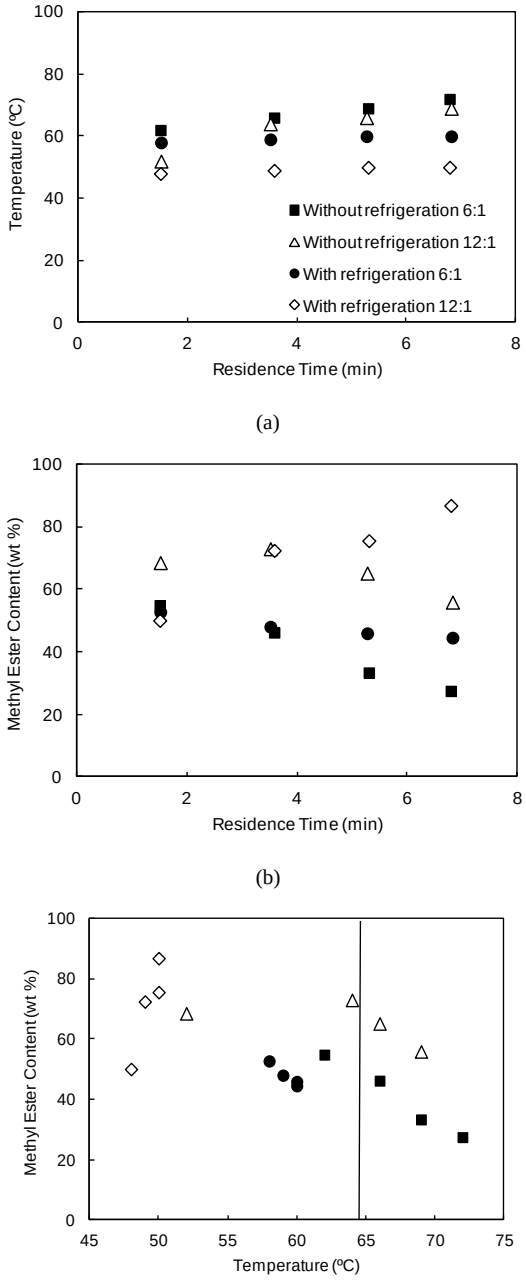


Fig. 7. Methyl ester content and temperature depending on the residence time for reactions in continuous processing with different MeOH:oil molar ratio and with and without refrigeration.

In this set of experiments, the highest ester content was achieved with 12:1 as MeOH:oil molar ratio and applying refrigeration. So four extra runs were carried out with 15:1 as MeOH:oil ratio, refrigeration and different residence times. The obtained results were drawn in Fig. 8 to compare them with other alcohol: oil molar ratios. This comparison

led to conclusion that molar ratios higher than 12:1 did not benefit the progress of the reaction.

The last set of experiments shows the effect of catalyst concentration on the ester content using several residence times. The results were shown in Fig. 9.

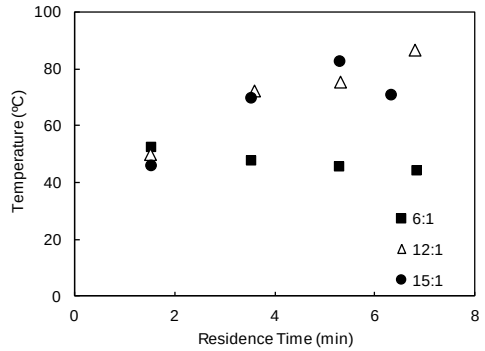
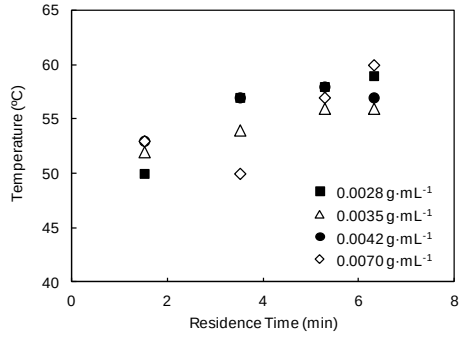
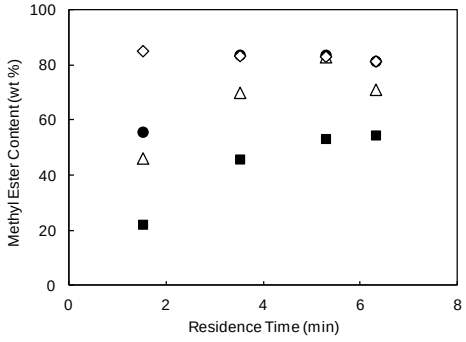


Fig. 8. Methyl ester content depending on the residence time for reactions in continuous processing with different MeOH:oil molar ratio.



(a)



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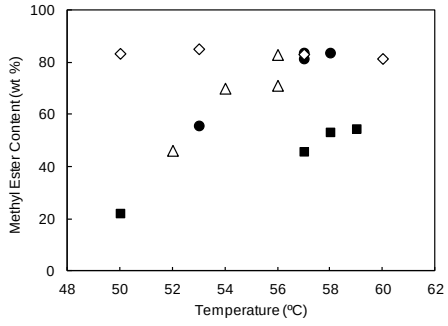

(c)

Fig. 9. Methyl ester content and temperature depending on the residence time for reactions in continuous processing with different potassium hydroxide concentration.

As residence time increased, temperature of the medium also increased for all of the catalyst concentrations.

In Fig. 9b and Fig. 9c, the effect of potassium hydroxide was shown. The highest ester content was achieved with the highest catalyst concentration, regardless of residence time and temperature.

IV. Conclusions

Biodiesel with high ester content was obtained assisted by ultrasonic irradiation. It is possible to use batch processing or continuous processing. In the batch process, if MeOH:oil molar ratio is increased, higher ester content will be achieved, although the reaction will be slower. On the other hand, the more power, the better results.

In the continuous process, a refrigeration system should be applied and MeOH:oil molar ration and catalyst concentration should be optimized. In this way, high methyl ester content and short reaction time could be managed.

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