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Molecular Distillation Process for Recovering Biodiesel and Carotenoids from Palm Oil

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Abstract

Carotenoids and biodiesel from palm oil were recovered through a process involving neutralization and transesterification of palm oil followed by molecular distillation of the esters. The concentrated obtained contains more than 30,000 ppm of carotenoids and the distillate contains above 95% of light-colored biodiesel. The experimental data were obtained from falling film and centrifugal molecular distillators. It can be seen that each one has its own characteristics, which are a function of the operating temperatures and of the tendency of the material thermal decomposition. These characteristics can determine the type of equipment to be used, since they have different operating conditions. The experimental results were compared to the ones from simulations using the mathematical modeling for the falling film and centrifugal distillators developed.

Index Entries: Molecular distillation; carotenoids; biodiesel; palm oil.

Introduction

Biodiesel has to be seen as an energy alternative with the advantage of being renewable. However, nowadays, the complete substitution for diesel is not possible due to its high cost and also due to the fact that it does not have complete adaptation of its use to the conventional diesel motors *(1)*. Its immediate application would be in the blend with diesel, with values that can reach up to 30%.

In this work, we are showing a process of molecular distillation in which one of the streams is rich in biodiesel (98–99% in weight) and

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another one is rich in β-carotenes (approx 30,000 ppm). The raw material used is palm oil.

It is known that palm oil contains a high concentration of natural carotenoids ranging from 500 to 3000 ppm depending on the species of the palm fruit from which the oil is obtained. The major carotenoids of the palm oil are α- and β-carotenes. Together, they constitute more than 80% of the total carotenoids in the palm oil. The β-carotene, in particular, and, to a lesser extent, α-carotene, are known for their provitamin A activities, as they are transformed into vitamin A in vivo *(2,3)*.

Most of the carotenoids in palm oil are destroyed in the conventional refining process to produce light-colored oils. This represents the loss of a potential source of natural carotenoids. The importance of carotenoids is well documented, and various methods of extraction and recovery from palm oil have been developed. These include extraction by saponification, adsorption, and transesterification followed by molecular distillation and other processes. However, only the transesterification and distillation processes have been developed into a commercial-scale process *(2)*.

This paper presents a suitable process to recover carotenoids and, consequently, the biodiesel from palm oil through transesterification and molecular distillation using falling film and centrifugal molecular distillators. The results were also evaluated in function of the type of molecular distillation equipment used and their operating conditions.

Finally, experimental results were compared to results from simulations using the mathematical modeling developed for both molecular distillators, showing the potentiality of this process for recovering biodiesel and carotenoids.

Methodology

Palm oil can be used as raw material for production of both provitamin A (carotenes) and biodiesel through the molecular distillation process. However, the palm oil cannot be used in its natural form, because it is comprised compounds of high molecular weight, such as triglycerides, therefore requiring higher temperatures in the molecular distillation processes, which can decompose the carotenes. Then, by a transesterification reaction with ethanol, triglycerides can be reduced to biodiesel, permitting the carotenes to be concentrated. The raw material was prepared following the procedure described below.

Neutralization and Transesterification

Neutralization of the palm oil is necessary to carry out transesterification. The palm oil has, in its natural form, 2–3% of free fatty acids (FFA). After neutralization, the oil must have an acidity index smaller than 0.3% of FFA. The oil was transesterified with ethanol (with 10% excess of ethanol solution), catalyzed by 0.4 % (w/w) sodium ethoxide, at 60°C and 0.3 h,

obtaining biodiesel. So, biodiesel was then separated from glycerol and washed with distillated water up to pH 6–8. Biodiesel was dried under reduced pressure by evaporation. This is the last stage of the preparation of the raw material before performing the molecular distillation, and it has the function of transforming the triglycerides to ethyl esters, which are easily removed by the molecular distillation process, because they have vapor pressure greater than the triglycerides. The conversion was above 94% in ethyl esters, making possible the use of molecular distillation.

DISMOL Simulator

DISMOL simulator was developed by the authors *(4,5)*. This simulator permits changing the feed composition, feed temperature, evaporation rate, as well as feed flow rate in order to find the best operating conditions. The liquid film thickness is solved by mass balance taking into account the geometry of the evaporator. The temperature in the liquid obeys the Fourier–Kirchhoff equation. The solution of the velocity profile requires the knowledge of the viscosity and the liquid film thickness on the evaporator. The calculations of the temperature and of the concentration profiles require the knowledge of the velocity profiles which determine the convective heat and mass fluxes. The vapor phase is modeled through a Monte Carlo method *(6)* considering the gas dynamic. For more details, see *(4,5)*.

Experiments of Molecular Distillation

Using the biodiesel obtained as described, the experiments for the molecular distillation were organized according to the following steps. Simulations were made to provide the best conditions for carrying out the experiments. These best values are related with the best performance of the process. So, experiments fixing the heating temperature and varying the feed flow rate were carried out. The feed concentration is fixed and the process pressure must be the smallest possible. The feed stream shows the following composition: 94.33% of biodiesel, 5% of triglycerides, 100 ppm of tocopherols, and 600 ppm of carotenes. It was used for the composition analysis a HPLC from Perkin-Elmer, with two columns: one of 100 Å and the other of 500 Å. For the carotene analysis an ultraviolet spectrophotometer from Perkin-Elmer was used.

Falling Film Distillator

The falling film molecular distillator used is shown in Fig. 1. The main part of the installation consists of a cylindrical evaporator and an internal condenser. The liquid to be distillated is transported from a storage tank (DO) through a degasser (DG) to the surface of the heated evaporator. It is also possible to operate adiabatically the evaporator. In this case, the distillation rate is smaller but the separation factor increases *(7)*.

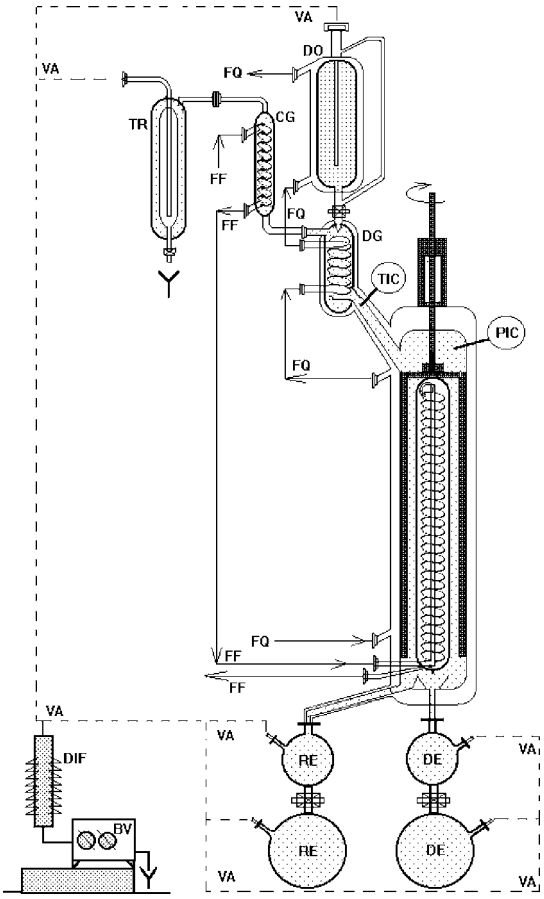

Fig. 1. Molecular distillator: falling film (Normschliff–Gerätebau).

The distillate flow rate is collected in the container DE, and the concentrated is carried to the container RE. The evaporator length is equal to 0.4 m, the evaporator radius is equal to 0.1 m, and the distance between the evaporator and the condenser surfaces is equal to 0.02 m.

Centrifugal Distillator

The centrifugal molecular distillator used is shown in Fig. 2. The liquid to be distillated is heated until the feed temperature and goes up to the evaporator center through pumping. The liquid flows by centrifugal force, uniformly around the evaporator, until the border of the rotor in a thin film where it is partially vaporized. It is possible to operate the equipment using reflux *(8)*.

The rotor diameter (evaporator) of the centrifugal distillator is 3 in., from Myers Vacuum Inc. Both equipment, falling film and centrifugal, enable efficient energetic integration with the possibility of using heated feed flow with temperature near the evaporator temperature.

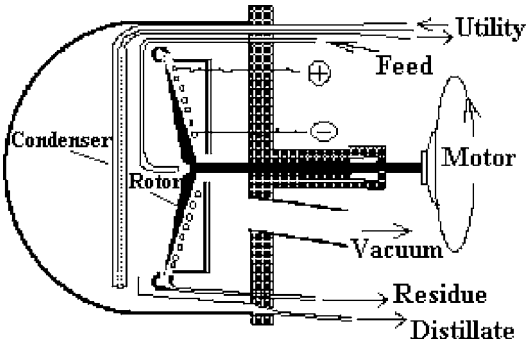

Fig. 2. Molecular distillator: Centrifugal (Myers-Vacuum).

Results

Falling Film Molecular Distillator

Distillations were carried out at pressure of 1×10^{-3} mmHg with temperatures ranging from 150 to 170°C, and feed flow rates between 0.6 and 2.1 kg/h. The initial carotene concentration was 600 ppm. The concentrate, rich in carotenes, was collected as the residue. The amount of the biodiesel was collected as the distillate.

So, for each liter of palm oil, approx 0.95 L of biodiesel and from 0.02 to 0.05 L of concentrated carotene (with up to 35,000 ppm of carotenes) are produced, beginning with a palm oil containing 630 ppm of carotenes. The neutralization stage loses near 3% of the initial palm oil mass.

Thus, the esters can be practically all removed from the feed stream, thereby concentrating the carotenes via molecular distillation. The distillated stream contains, at least, 98% of biodiesel (ethyl esters) with the following composition: 44% of ethyl palmitate, 37% of ethyl oleate, 10% of ethyl linoleate, 4% of ethyl stearate, and 3% of ethyl of other acids, as for example, palmitoleic. The generated biodiesel presents light color, similar to the refined soya oil. Here, the focus was on the carotenoid recovery, this one much more thermally sensitive than biodiesel. The biodiesel recovery is easier and simpler.

The experimental results were compared with the simulation results. The results are shown in Figs. 3–5.

It can be verified in Fig. 3 that when the process temperature increases, the concentration of carotenes increases too, for the same flow rate. Considering a feed flow rate of 1.2 kg/h, at 150°C, the concentration obtained was 4500 ppm; at 160°C, the carotene concentration was 25,000 ppm, and at 170°C, the concentration was 35,000 ppm. Considering the tests changing only the flow rate, it can be seen that the concentration increases when the flow decreases. This is valid for each temperature considered.

Figure 4 presents the percentage of decomposition versus residence time. For all temperatures used, it can be seen that, increasing the residence time, the decomposition also increases, because the longer the

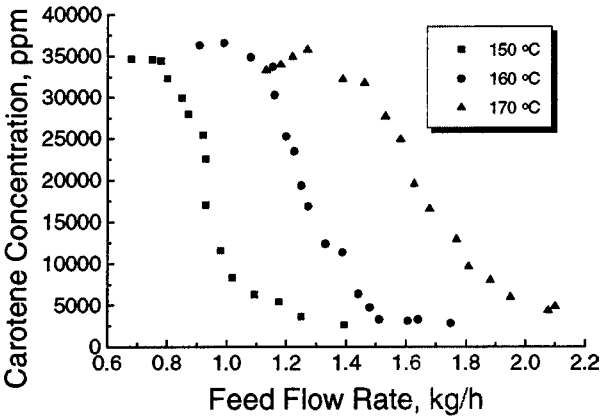

Fig. 3. Experimental carotene concentrations.

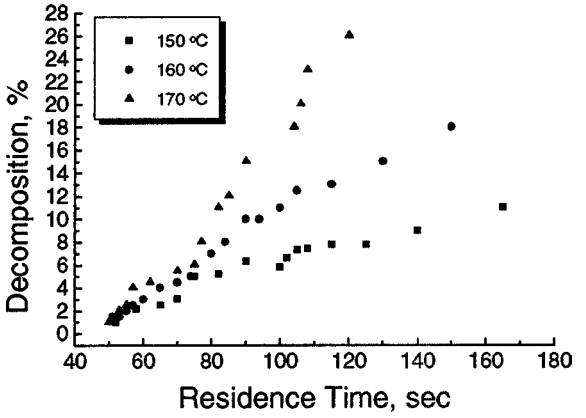

Fig. 4. Decomposition of carotenes for different temperatures and residence times.

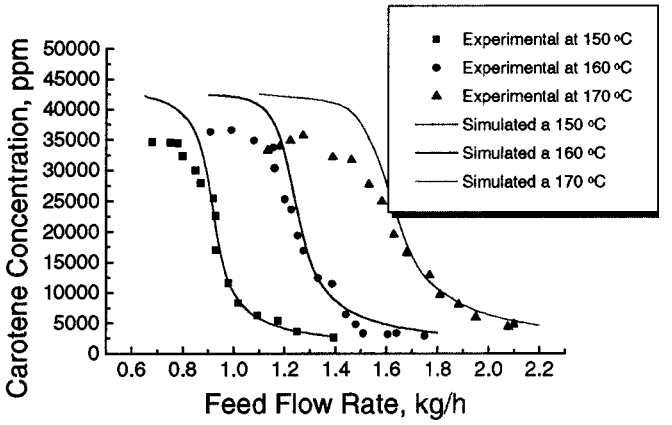

Fig. 5. Experimental versus simulated carotene concentrations.

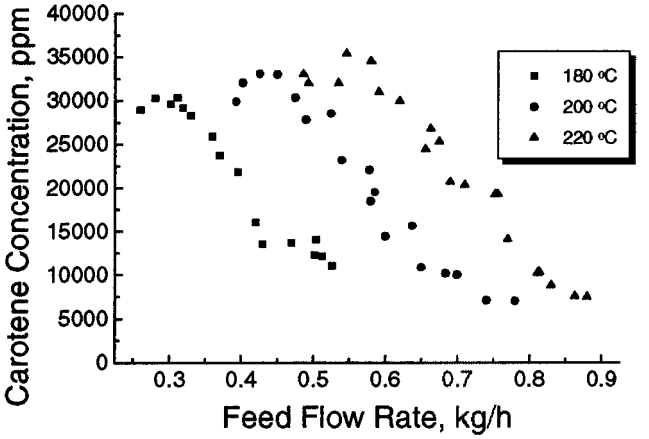

Fig. 6. Experimental carotene concentrations.

evaporation time is, the longer is the heating, decomposing the carotenes. On the other hand, when the feed flow rate increases, the decomposition of carotenes decreases, because the exposure time on the heated evaporator decreases. To see the comparison of the experimental and simulated results for all temperatures used, refer to Fig. 5. When the carotene concentrations by simulation and by experiments are analyzed in Fig. 5 (it is necessary to neglect the thermal decomposition, because the simulator does not take this fact into account), it can be seen that for lower values of the feed flow rate there are some deviations. This is due to thermal decomposition. Including this variable in the model is a complex task (but it is possible), because it is necessary specific experimental data for adjustment.

For higher feed flow rate, good agreement between simulated and experimental data is achieved enabling to establish operating conditions for the process.

Centrifugal Molecular Distillator

Distillation was carried out at pressure of 1×10^{-3} mmHg with temperatures ranging from 180 to 220°C, and feed flow rate between 0.25 and 0.9 kg/h. Other details of the operating conditions are the same as the falling film experiment.

Similar to the falling film distillation, the concentrate, rich in carotenes, was collected as the residue. The amount of the biodiesel was collected as distillate. Therefore, each liter of palm oil will generate, at least, 0.95 L of biodiesel and from 0.02 to 0.05 L of the carotene concentrate, with up to 37,000 ppm of carotenes. The results are shown in Figs. 6–8.

The same tendency of the falling film distillator can be verified in Fig. 6, i.e., the concentration of carotenes is a direct function of temperature. However, it is convenient to mention that the ranges of temperature and feed flow rate are not equal in both equipment. This is because these

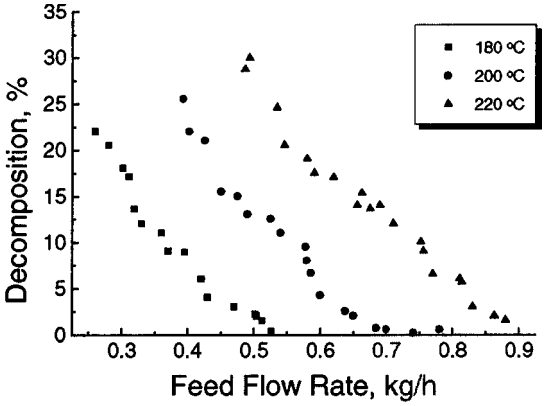

Fig. 7. Decomposition of carotenes for different temperatures and feed rates.

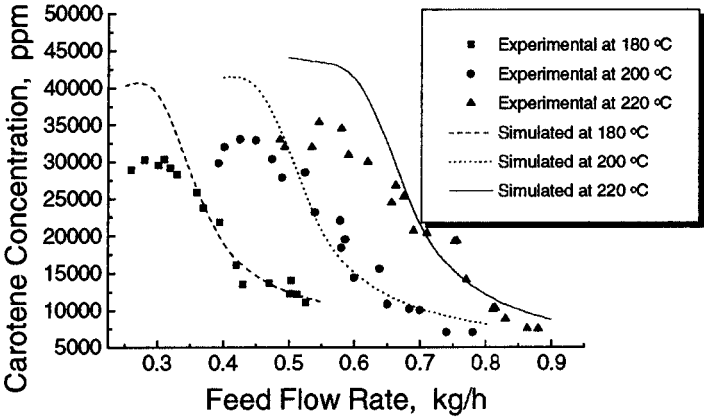

Fig. 8. Experimental versus simulated carotene concentrations.

ranges were chosen as a function of the decomposition index and of the considerable concentration value of carotenoids obtained.

Figure 7 shows the same problem of decomposition. Increasing the feed flow rate results in a smaller decomposition. In Fig. 8, it is possible to compare the simulated and the experimental data for the concentration of carotenoids. The figure shows that simulation results approach the experimental data for higher values of feed flow rate, because the thermal decomposition for smaller values according to Fig. 7.

Comparison Between Falling Film and Centrifugal Distillators

A comparison between the falling film and centrifugal distillators is shown in relation to the decomposition level as functions of the process temperature and experimental concentration of carotenes. Figure 9 shows the decomposition curves of the falling film and Fig. 10 shows the decomposition curves of the centrifugal distillator. It can be seen, for both equipment, that for obtaining a fixed concentration of carotenoids, the

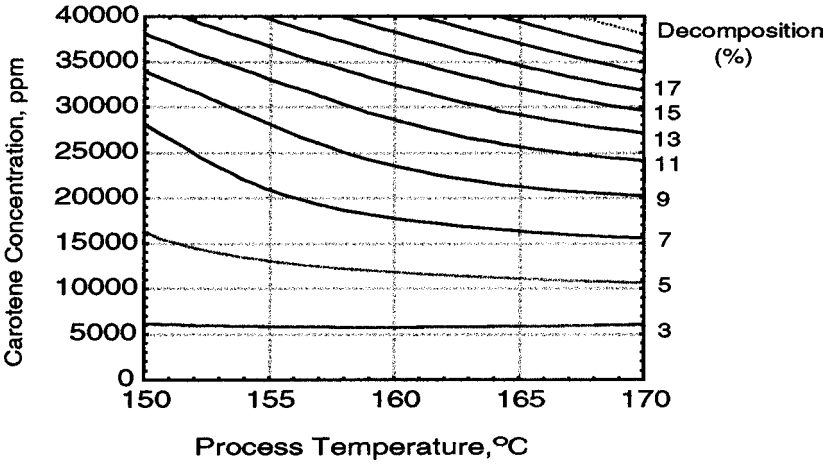

Fig. 9. Decomposition levels for the falling film distillator.

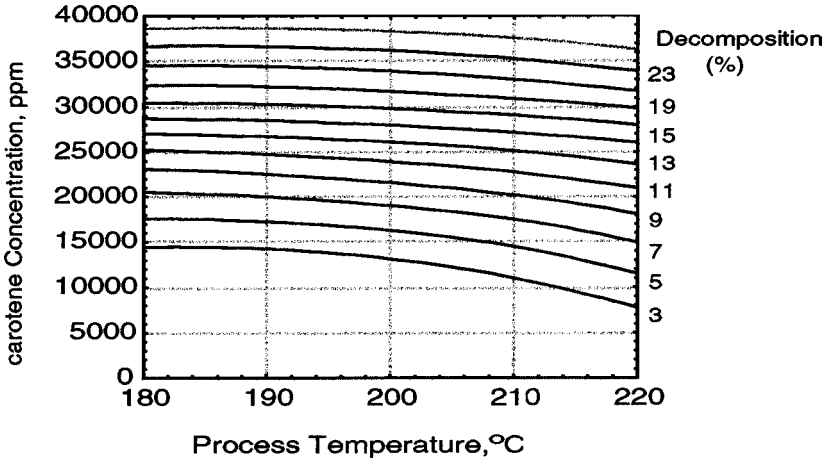

Fig. 10. Decomposition levels for the centrifugal distillator.

decomposition increases, increasing the temperature. However, this is much more significant for the falling film distillator. An example of concentration of 25,000 ppm, with the falling film at 150°C, there is a decomposition of 6.5% and at 170°C (20°C above) of 11.5%. Using the centrifugal distillator at 190°C, the decomposition is 12% and at 210°C is 13%.

Then, it can be seen that carotenoids are less thermally sensitive at low temperatures (150°C) (minimum decomposition), but, on the other hand, they are strongly sensitive at high temperatures, even at a short residence time (centrifugal distillator). Therefore, in this case, it is more interesting to operate with a falling film, at low temperatures, in order to decrease the index of carotene decomposition. On the other hand, biodiesel is not thermally sensitive.

Concluding Remarks

In this work, the study of a process which produces simultaneously β-carotenes and biodiesel is presented, and we have compared two types of molecular distillators. For each kilogram of palm oil, it is possible to obtain 20 g of β-carotene with a concentration of about 30,000 ppm. The biodiesel was obtained with high concentration of ethyl esters (above 98% in mass fraction) besides being almost clear and containing reduced amounts of monoglycerydes (smaller than 1%) and practically being free of di- and triglycerydes, evaluated by HPLC analysis, according to the procedure described in this work.

The molecular distillation technique provided excellent carotenoids recovery, with high concentrations. Considering the recovery of carotenoids, the performances of the falling film and of the centrifugal molecular distillators, in general, decrease when the residence time is large, owing to the thermal decomposition of carotenoids. The same happens with the increase in the distillation temperature. It can be said that the process used in this work enables the recovery of carotenes with concentrations above 30,000 ppm. This is an important achievement considering the high value of this material.

Comparing the performance of both distillators, falling film and centrifugal, the distillation time of the first one is larger (40 times), since the centrifugal force increases the velocity of the distilling liquid. Therefore, the falling film distillator can operate with a comparatively lower temperature than the centrifugal distillator, and at the end of the distillation, the amount of the distillate is the same. On the other hand, a disadvantage of the falling film is that the time of exposition being larger can lead to component decomposition. It is necessary to say that the main goal here is to verify the behavior of molecular distillation, for both equipment, for recovering carotenoids, and for obtaining biodiesel, besides comparing the two kinds of stills in function of the obtained concentration and level of carotenes decomposition. The process optimization would be an another step of study, not presented here.

Finally, the use of the DISMOL simulator can calculate the feasibility and flexibility of the process for a given system, the performance of the process, as well as the best operating conditions to carry out the experiments. These can represent a substantial reduction in the experimental time and a process development, and, finally, it is possible to optimize it, through simulations.

Acknowledgments

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