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Simulation and Optimization of a Supercritical Extraction Process for Recovering Provitamin A

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Abstract

In this work, a simulation procedure of a supercritical extraction process was developed through the use of the commercial simulator HYSYS™ (Hyprotech Ltd.), adapting the existing units to the operating conditions typical of the supercritical extraction process. The objective is to recover provitamin A (β-carotene) from palm oil (esterified) using carbon dioxide/ethanol as the supercritical mixed solvent. This example characterizes the problem for recovering high added value product from natural sources, as the palm oil, which is desired by the market. Owing to the fact that esterified palm oil is a complex mixture, made by several components, in order to characterize this system in the simulator, it was necessary to create hypothetical components using the UNIFAC (universal function-group activity coefficients model) group contribution, because they are not present in a conventional database and, then, their physical properties must be estimated and/or predicted before the simulation. The optimization was carried out in each simulation for each equipment, in terms of operating conditions (temperature and pressure), in order to obtain the maximum recovery of carotenes. According to the results, it was possible to concentrate carotenes through two cycles of supercritical extraction with high yield. Furthermore, ethyl esters (biodiesel) were also obtained, as a byproduct of the proposed process, which can also be used as an alternative fuel, with the important characteristic that it is renewable.

Index Entries: Biodiesel; carotenes; palm oil; supercritical extraction.

Introduction

The supercritical extraction process represents an alternative to conventional separation methods, especially in treating and processing natural compounds like, for example, vitamins *(1)* because of the favorable

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properties of supercritical fluids, such as solvent recovery, simple separation, favorable thermal conditions and mass transfer properties, and solvent-free products.

CO_2 is the most commonly employed solvent, because it is relatively inert, cheap, nontoxic, recyclable and nonflammable and its critical properties (critical pressure = 7.37 MPa and critical temperature = 30.95°C) are easily reachable. The use of cosolvent, as the ethanol in the present work, is also possible, in order to improve the separation. However, the solvent choice depends on the system.

An extensive description of the properties of supercritical fluids, as well as an overview about SFE application is given in ref. 2.

Palm oil is the major edible oil in the south-east Asian region and has the second place in the world, after soy oil. The first step in palm oil processing is at the mill, in which the crude palm oil is extracted from the fruit. The oil extraction follows various steps: sterilization in large pressure vessels, stripping in rotating drum, extraction in a homogeneous oil mash, and purification in a continuous clarification tank. The oil is bright orange-red because of the high content of carotenoids *(3)*.

Carotenoids are divided into two groups: carotenes and xanthophylls. Although carotenes are purely hydrocarbons, xanthophylls are oxygenated at the ends groups and as a result they are polar. The type and amount of pigment in vegetable oils depend fundamentally on the species, cultivars, state of ripeness, and agronomic conditions, and so on, and, in general, undergo a considerable variation during storage and preparation as edible oils *(4)*.

Carotenoids, in particular β-carotene, are one of the major groups of natural pigments that find widespread utilization in the food industry. Addition of β-carotene to foods imparts a uniform color and some vitamin A activity. As many vegetables are sources of carotenoids, they offer the possibility of obtaining natural pigments, provided that a nontoxic extraction technology is used. β-Carotene is a hydrocarbon of 40 carbon atoms, a lipid-soluble, yellow to orange–red pigment, and highly unsaturated, as it contains 11 conjugated carbon–carbon double bonds *(5)*. It is illustrated in Fig. 1.

In this work, an esterified palm oil was used as raw material, which means that the crude palm oil was esterified and, then, the glycerides were reduced to lighter components, as ethyl esters. Ethyl esters are also known as biodiesel, which has to be seen as an energy alternative with the advantage of being environment-friendly, biodegradable and renewable.

It is a simulation of the supercritical extraction process with CO_2/ethanol as supercritical solvent, using the HYSYS™ commercial simulator.

Methodology

It is known that the palm oil contains a high concentration of natural carotenoids, in the range of 500–3000 ppm, depending on the species of the palm fruit, which the oil is obtained.

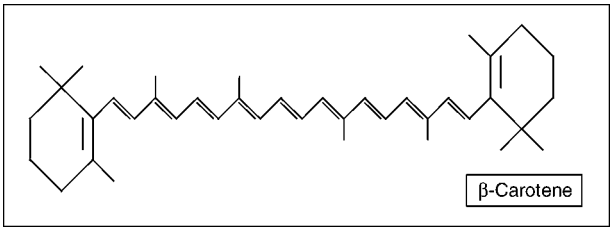

Fig. 1. Molecular structure of β-carotene.

The majority of the carotenoids in the palm oil are destroyed in the conventional refining process for producing clear oil. This represents a loss of the natural source of carotenoids. The importance of the carotenoids is well reported in the literature and some methods of extraction and recovery, from the palm oil, have been developed. This includes extraction by saponification, adsorption, and transesterification followed by molecular distillation and others. However, only transesterification processes and distillation have been fully developed in the commercial scale processes *(6)*. Batistella et al. *(7)* has studied the recovery of biodiesel and carotenoids through the molecular distillation process.

Palm oil can be used as raw material for production of provitamin A (carotenes), but not in its natural form. It is necessary to carry out a transesterification reaction, which can reduce the glycerides in lighter components, as ethyl esters. So, after transesterification, the esterified palm oil is rich in ethyl esters and carotenes, whereas before, the crude palm oil was rich in triglyderides and carotenes.

Glycerides react with ethyl alcohol through a basic catalysis, producing ethyl esters. The chosen process of transesterification presents innumerable advantages in relation to other processes, as for example, the fermentative. This last one needs enzymes of difficult attainment and raised price, besides presenting high times of process. The chosen process presents high conversion rate, even for small reaction time. Reactions in reduced time, such as 15 min, present a conversion in ethyl esters of, approx 94%. The conversion of the triglycerides, a compound that has a larger molecular weight, reaches the levels of 98% in this same time, as it is presented ahead. The methodology for the preparation of the raw material is described in the following sections.

Neutralization of the Palm Oil

The crude palm oil presents, normally, 2–3% of free fatty acids (FFA). These acids represent an enormous problem in the transesterification reaction, because they deactivate the used catalyst. So, the FFA must be reduced from the palm oil to values of 0.3%. The adopted process is the controlled saponification (the neutralization of these acids) and the removal of the soaps by centrifugation. After this removal, the palm oil is washed, treated

with Sorbamol™ (Süd Chemie AG) (which is an adsorbent that removes soap residues, phosphorous, and metallic particles of the oil), and it is dried by evaporation at reduced pressures. After the drying, the oil is filtered to remove the sorbamol used.

The yield was 98%, and the loss of carotenes was 3%. The neutralization of the palm oil, for this process, reduced the acidity in 0.2% of FFA, becoming possible to use the oil for the transesterification reaction, the next stage of preparation of the raw material.

Transesterification

This is the final step of preparation of the raw material and it has the purpose to transform the palm oil, which is rich in glycerides, to lighter components, as ethyl esters (biodiesel).

Because it is the last step, the oil must be without solid materials, volatiles and soap (elements present in the preparation processes), the conversion to ethyl esters must be high and the carotenoids loss must be minimum.

After neutralization, 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 ethyl esters and glycerol. The ethyl esters were, then, separated from glycerol by decantation, washed with distillated water up to pH 6.0–8.0 and dried under reduced pressure by evaporation. The conversion was above 94% in ethyl esters. The obtained oil is denominated esterified palm oil.

Components Creation and Methodology for Simulation

Esterified palm oil is a complex mixture made by several complex components, and it is very hard to find their physical properties in a conventional simulator database. First, it was necessary to create in the simulator hypothetical components, which take into account the structure of the molecules, in order to be possible to count the groups and the number of groups present in each molecule according to the methodology presented in the software, using the UNIFAC group contribution (a tool of the commercial simulator HYSYS). So, they are automatically introduced in the simulator database and the physical properties can be predicted. After creating, the components can be used to simulate the process in the simulator HYSYS. Furthermore, it was necessary to adapt the existing units in the simulator to simulate the supercritical extraction process. In the HYSYS database, the thermodynamic package that was chosen was the EOS-Peng-Robinson to represent the vapor phase and an activity coefficient model (UNIQUAC [universal quasi-chemical model]) to represent the liquid phase. For this study, the components used are described *(8)*, in Table 1.

The unknown binary coefficients, a_{ij}, which are the nontemperature-dependent energy parameter between components *i* and *j*, of the UNIQUAC

Table 1
Esterified Palm Oil Composition Used in the Simulation

Components	Mass (%)
Ethyl palmitate	42.3
Ethyl oleate	37.6
Ethyl stearate	3.76
Ethyl linoleate	10.34
β-carotene	0.06
α-tocopherol	0.01
Tripalmitin	0.69
Triolein	0.69
Dipalmitin	0.94
Diolein	0.93
Monopalmitin	1.34
Monoolein	1.34
Total	100

activity coefficient model were estimated through UNIFAC vapor-liquid equilibrium. The automatic UNIFAC generation of energy parameters in HYSYS is a very useful tool and it is available for all activity models. By default, HYSYS regresses only the a_{ij} parameter, whereas the b_{ij}, the temperature dependent energy parameter between components i and j, is set equal to 0.

To make the extraction, an absorber column was used as unit operation present in the simulator, called here as "extractor." The solvent was the supercritical CO_2/ethanol mixture and the feed was made by the components presented in Table 1 (esterified palm oil). The design and operating variables are described in Section 3.

Results and Discussions

A diagram for the supercritical extraction process was proposed for provitamin A recovering from the esterified palm oil, as it can be seen in Fig. 2. At this point, it is important to remember that ethyl esters (biodiesel) are also one of the components to be considered in the simulation. The mass flow rates of the main streams are presented in Table 2.

The first extractor has 10 stages and operates at pressure (P) = 30 MPa. The temperature of the feed is 100°C and the mass flow rate is 100 kg/h. The temperature of the solvent (CO_2/ethanol) is 100°C and the mass flow rate is 800 kg/h in the proportion 80/20 (640/160 kg/h).

Analyzing the first extractor, as can be seen in Table 2, the raffinate stream (bottom extractor) is composed by a phase that is rich in beta-carotene (0.06 kg/h), tocopherol (0.01 kg/h), ethyl esters (47.72 kg/h), mono- (2.52 kg/h), di- (1.87 kg/h), and triglycerides (1.38 kg/h). In the

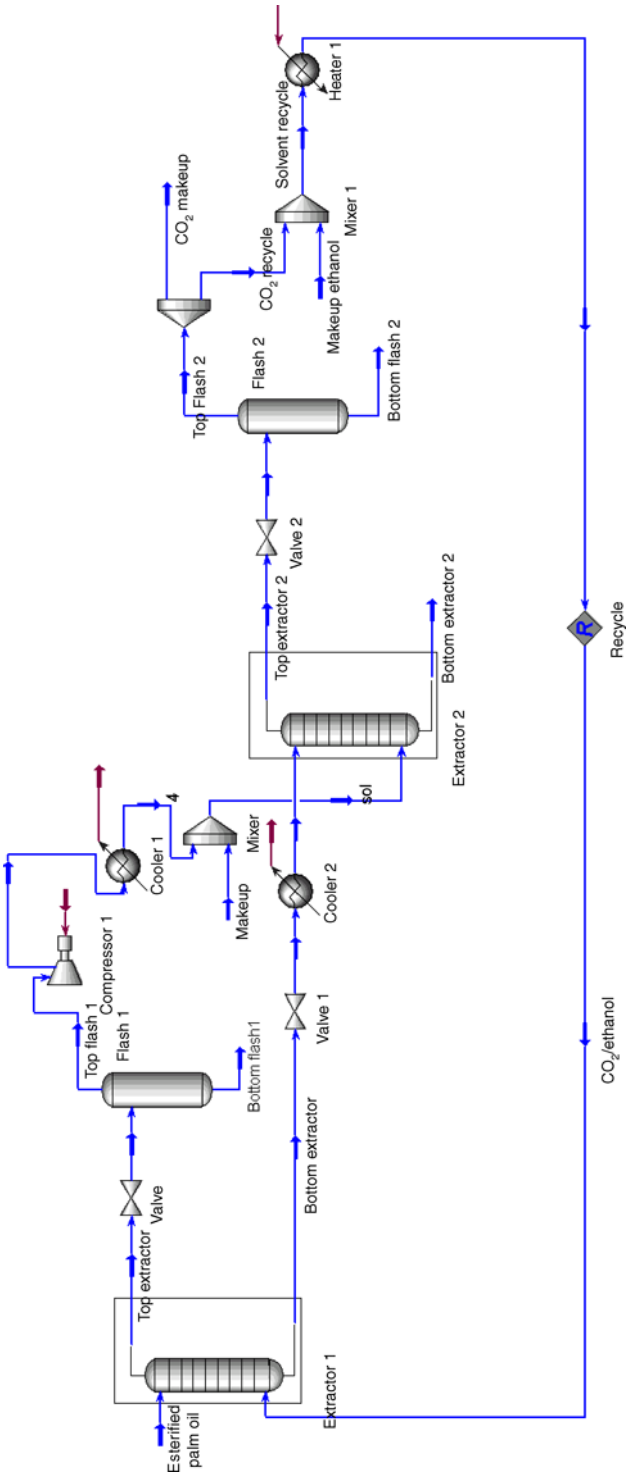

Fig. 2. Proposed process flow diagram for recovering provitamin A from esterified palm oil.

Table 2
Simulation Results of the Supercritical Extraction Process for Provitamin A Recovering From the Esterified Palm Oil

Components	Feed flow rate (kg/h)	Top extractor Mass flow rate (kg/h)	Bottom extractor Mass flow rate (kg/h)	Bottom flash 1 Mass flow rate (kg/h)	Bottom extractor 2 Mass flow rate (kg/h)	Bottom flash 2 Mass flow rate (kg/h)
Ethyl palmitate	42.3	25.89	16.41	25.88	0	16.41
Ethyl oleate	37.6	14.57	23.03	14.57	0	23.03
Ethyl stearate	3.76	1.26	2.5	1.26	0	2.49
Ethyl linoleate	10.34	4.56	5.78	4.56	0	5.78
β-carotene	0.06	0	0.06	0	0.06	0
α-tocopherol	0.01	0	0.01	0	0	0.01
Tripalmitin	0.69	0	0.69	0	0.69	0
Triolein	0.69	0	0.69	0	0.69	0
Dipalmitin	0.94	0	0.94	0	0.94	0
Diolein	0.93	0	0.93	0	0.93	0
Monopalmitin	1.34	0.11	1.23	0.11	0	1.23
Monoolein	1.34	0.05	1.29	0.05	0	1.29
Total (streams)	100	46.44	53.56	46.43	3.31	50.24
CO_2 (solvent)	640	635.58	4.42	6.46	0	5.66
Ethanol (solvent)	160	128.69	31.31	99.35	0.24	51.54
Total (solvent)	800	764.27	35.73	105.81	0.24	57.2
Total (streams + solvent)				152.24	3.55	107.44

extract stream (top extractor), there is a phase that is rich in the supercritical solvent CO_2/ethanol (635.58/128.69 kg/h), ethyl esters (46.28 kg/h) and monoglycerides (0.16 kg/h). As the carotenes are in the rafinatte stream of the first extractor (bottom extractor) with a great quantity of ethyl esters, it will be necessary another extractor in order to separate these components. So, this stream passes through a valve to reduce the pressure to 20 MPa and, later, it passes through Cooler 2 to reduce the temperature to 100°C and it will be used as the feed of extractor 2.

On the other hand, the top stream of extractor 1 (top extractor) passes through a valve to reduce the pressure to 6.5 MPa and goes to flash 1. At the top of the flash (top flash 1), there is the solvent CO_2/ethanol (629.13/29.34 kg/h) and at the bottom (bottom flash 1), there are ethyl esters (46.27 kg/h), monoglycerides (0.16 kg/h) and a bit of solvent (6.46/99.35 kg/h). This stream passes, then, through a compressor (compressor 1) to reach the pressure equal to 20 MPa, after through cooler 1 to reduce the temperature to 100°C and, later, goes to mixer for its future use in extractor 2. In this mixer, a make-up of solvent CO_2/ethanol (22.5/2.5 kg/h) is carried out.

The rafinatte stream of the first extractor (bottom extractor) feeds the extractor 2 and the stream of the top of the flash 1 (top flash 1) is used to offer the necessary quantity of solvent (651.63/31.84 kg/h) for carrying out the second extraction.

Extractor 2 has also 10 stages and operates at 20 MPa. At the top of extractor 2 (top extractor 2), there are ethyl esters (47.72 kg/h), tocopherol (0.01 kg/h), monoglycerides (2.52 kg/h), and the solvent CO_2/ethanol (656.04/62.91 kg/h), whereas that at the bottom of extractor 2 (bottom extractor 2), there are β-carotenes (0.06 kg/h), di- (1.87 kg/h) and triglycerides (1.38 kg/h). This stream (bottom extractor 2) is important because beta-carotenes can be concentrated.

The top stream of extractor 2 (top extractor 2) passes through a valve to reduce the pressure to 6.5 MPa and goes to flash 2. At the top of the flash (top flash 2), there is the solvent CO_2/ethanol (650.38/11.37 kg/h) and at the bottom there are ethyl esters (47.72 kg/h), tocopherols (0.01 kg/h), monoglycerides (2.52 kg/h), and a bit of solvent (5.66/51.54 kg/h). The stream top flash 2 is divided: one part goes to solvent recycle (640.06/11.19 kg/h) and the other one (10.32/0.18 kg/h) to a possible use in the make-up of solvent. This divisor must be used in order to reuse the solvent. This stream must be identical to the initial solvent stream, that is 640 kg/h of CO_2/160 kg/h of ethanol. So, this procedure avoids any problem with the recycle closing. As the part of the solvent recycle contains only a bit of ethanol, it is necessary to introduce a make-up of ethanol (148.9 kg/h), using a mixer (mixer 1). Then, it is already possible to have the initial proportion of 80/20 of CO_2/ethanol. Moreover, this stream (solvent recycle) passes through a heater to increase the temperature to 100°C and the pressure must be 30 MPa. Thus, the solvent stream

is ready to be reused in extractor 1, closing the recycle, in order to reinitialize the process.

As can be verified in Table 2, in bottom extractor 2 stream, it was possible to concentrate β-carotenes. There are also di- and triglycerides, which come from the nonconversion fraction in the transesterification process, that remain with the carotenes, what is already expected because of similar characteristics among these components. The recovery and the purity in relation to the composition of the feed and the total mass flow of this stream can be calculated. As a result, carotenes can be recovered from esterified palm oil until 16,900 ppm that is, about 28 times in relation to the feed (600 ppm of carotenes). The recovery was about 100.00%.

The optimization was carried out in each simulation for each equipment, in terms of operational conditions (temperature and pressure), in order to obtain the maximum recovery of carotenes.

Because other interesting product was obtained, the ethyl esters or biodiesel, as a byproduct, it will be calculated the recovery and the purity in relation to the composition of ethyl esters in the feed (94 kg/h) and the total mass flow (259.68 kg/h) of the two streams, bottom flash 1 and bottom flash 2, that are rich in ethyl esters (93.98 kg/h). The recovery was of 99.98% and the purity of 36.19%, because of the presence of tocopherols (0.01 kg/h), monoglycerides (2.68 kg/h) and, also, solvent (12.12/150.89 kg/h). According to these results, it was possible to concentrate carotenes through two cycles of supercritical extraction. Biodiesel was also obtained, as a byproduct of the proposed process, which can be also used as an alternative fuel, with the important characteristic that it is renewable.

β-Carotene is a high added value product that may be obtained under specific operating conditions to have its properties preserved. This is especially true for temperature, so that it is imperative the use of process development taking into account such constraint. Supercritical extraction is a process, which fits well in such situation as shown for β-carotene in this work and for tocopherol and phytosterol recovery from deodorizer distillate of soy oil *(9)*. A question commonly concerned to supercritical extraction process is that related to its cost. However, this is not a restriction for recovering valuable products with clean technology. In fact, for the case of vitamin E a rough product cost estimation leads to a value about half of the market price, and taking this into consideration as a basis, the value for the β-carotene is to be compatible and, in fact, very attractive for this case. It is worthwhile mentioning that the required quality is achieved without any addition of toxic chemical which is very much welcome. An interesting feature to be pointed out is the fact that in the developed process to obtain β-carotene is the production of the relatively valuable byproduct, to know, the biodiesel, which, in fact, leads to an additional gain in the process, as well as a significant decrease in environmental and energetic impacts, because a drastic reduction in the downstream treatment is achieved.

Conclusions

The results obtained in this work indicate that it is possible to concentrate carotenes approx up to 17,000 ppm, that is, about 28 times higher than the feed (600 ppm of carotenes). The recovery was about 100%. To accomplish this, two supercritical extractors in series were necessary what demonstrates the rigorous methodology used and its practical viability. Furthermore, the operating conditions were the typical ones encountered in supercritical process and the use of ethanol as cosolvent is very attractive, because it is a renewable source material. Moreover, with this study, it was observed that it was also possible to recover ethyl esters (biodiesel), with a recovery of 99.98% and a purity of 36.19%, considering the two streams that are rich in ethyl esters, what makes this process highly important, because the byproduct is a valuable material. This is a theoretical result, but extremely important in order to guide experimental works, both in terms of the rigorous calculations used and of the optimization conditions achieved for the design and operating variables.

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