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ORIGINAL ARTICLE

Industrially concentrated tocopherols from soybean oil deodorizer distillate

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Abstract

Although the tocopherol concentration in Soybean Oil Deodorizer Distillate (SODD) regarding molecular distillation (MD) has been studied in the last 20 years, no scientific studies were published yet in international journals about the results of this technology when applied in an industrial scale. This research aimed to evaluate the tocopherols concentration through industrial patented MD technology in a vegetable oil refinery, using a phospholipase A2 enzymatic physical degumming process, packed dual temperature column deodorizer coupled to a double washer and a Tocoboost® patented technology. The results of the refinery production process from July 2019 to February 2020 could totalize over 81 days, comprising 243 samples and more than 1900 laboratory analysis. The input and output SODD samples were analysed by Gas Chromatography (GC), in which graphics of the automation system and mass balance of the refinery production ranges were also verified. The results showed that it is possible to achieve over five times Vitamin E concentration from non-modified soybean oil deodorizer distillate in a physic enzymatic phospholipase degumming process plant using a combination of advanced technology in order to separate high value-added molecules gained through studied hypotheses regarding vacuum, temperature, distiller models, backset flows, multiple stages of distillation, degradation and product recovery.

Keywords: Purification; Bioactive compounds; Double scrubbers; De-acidification.

Highlights

- Industrial scale of molecular distillation patent for tocopherol content evaluation
- Over five times the concentration to physically refined soybean oil deodorizer distillate
- Strong statistical multivariate correlation with raw material micronutrients
- Maximum results for enzymatic degumming process plant product
- 528% of tocopherol was recovered with EP 2 597 142 A1 patent technology

1 Introduction

Vegetable Oil Deodorizer Distillate (VODD) is a multiple mixture of many healthful components as well as volatile compounds present in low concentrations that attribute undesirable odor, color and taste to refined oil (Sherazi & Mahesar, 2016). Soybean Oil Deodorizer Distillate (SODD) is one of these VODDs, and this method is constituted by the blend of free fatty acids (~73%), mono, di and triacylglycerols (~7.67), ketones, peroxides and hydrocarbons (not quantified), oleins (~4.45%), sterols (~6.32%) and tocopherols (~7.50%) (Benites et al., 2009).

There are others VODDs such as Corn Oil Deodorizer Distillate (CODD), Sunflower Oil Deodorizer Distillate (SuODD), Rapeseed oil Deodorizer Distillate (RODD), Olive Oil Deodorizer Distillate (OODD) and Palm Fatty Acid Distillate (PFAD). However, SODD is the VODD most studied in the literature because soybean oil is the most consumed vegetable oil in the world after palm oil (Gunawan & Ju, 2009).

SODD is a byproduct obtained from the soy oil deodorization process that occurs by steam dragging at high temperature and under vacuum conditions. These conditions prevent material oxidation by contact with oxygen, as well as its hydrolysis due to steam action (Benites, 2008). They are used in feed additives, as fluidizing agents for lecithin or as raw material for soaps (Torres et al., 2011) and for biodiesel production (Gunawan & Ju, 2009).

Deodorization is one of the steps in all vegetable oils refining that can be carried out in two ways: chemically and physically (Bezerra, 2021). The difference between refining types is the presence or absence of neutralization step in which physical refining is not carried out. Although the physical refining process is technically more expensive, its main advantage is environmental compatibility because the effluent is drastically reduced, whereas Free Fatty Acids (FFA) are recovered in the deodorization distillate and the refinery losses are lower (Martins et al., 2006).

The deodorization step is carried out in a high temperature steam drag distillation column, between 200 °C and 250 °C and with a vacuum of less than 10 mmHg, in which rise two streams columns: the bottom stream has refined soybean oil; and in the top stream SODD evaporates as Martins et al. (2006) described in their work.

SODD can be one of the main raw materials for vitamin E (tocopherol) extraction and recovery in edible oils as Solanki & Upadhyay (2018) reported. Tocopherol, the major constituent of Vitamin E, is a compound of the antioxidant membrane in mammalian cells that prevents the oxidation of vitamin A and β-carotene and they are essential fatty acids that can reduce risks of diseases such as cancer, cardiovascular diseases and severe cataracts (Ito et al., 2007).

In fact, the biological activity of the tocopherols is due to their antioxidant capacity (Liu et al., 2008) against lipid peroxidation in organic membranes, as their composition is capable of eliminating peroxyl radicals from their propagation chain. Tocopherol is a product with greater interest in SODD due to its high added value, its nutraceutical activities (Shao et al., 2007) and because it is a bioactive compound (Bezerra et al., 2020).

The greatest amount of natural Vitamin E is obtained during the refining of vegetable oils, mainly soybean oil and α-tocopherol are extracted and isolated directly from a vegetable source, with no modification (Jensen & Lauridsen, 2007). In this research, the evaluated SODD has no chemical modifications and this is one of the molecular distillation advantages (Malekbala et al., 2017).

Thus, short path or molecular distillation, is a suitable separation process for thermally unstable substances purification and separation, as well as for materials with high molecular weight and low vapor pressure, such as vitamins or FFA, reducing losses due to thermal decomposition (Japir et al., 2016). The evaporation temperature was the most important tocopherol recovery parameter in the distillate from canola oil deodorization (Jiang et al., 2016). As an efficient way of extraction, the molecular distillation approach is advised as an easier process to physically separate valuable compounds and due to high vacuum levels, higher purities can be accomplished as a result of using low evaporation temperatures (Ketenoglu et al., 2018).

In this research, the tocopherol values presented are related to total values, however, Zhan et al. (2020) could inform that tocopherols are divided into four types: α-tocopherol; β-tocopherol; γ-tocopherol; and δ-tocopherol. There are also derivatives such as α-tocotrienol, β-tocotrienol, γ-tocotrienol and δ-tocotrienol. Wu et al. (2020) found out in their research that Elaeagnus seed oil contains high content of α- and γ-tocopherols.

Therefore, this research aims to evaluate tocopherol concentration in SODD produced in a soybean oil physical refining plant through an enzymatic process of the phospholipase A2 type and molecular distillation technology registered by the company Alfa Laval installed in an industry located in the state of Goiás – Brazil (Figure 1).

Figure 1. Technology of Molecular Distillation. From the left to the right: Tocobooster, Deodorizer bellow and Double Scrubber above.

There are other technologies used in the separation and/or extraction of tocopherols and biocomponents such as super critical fluid (Mendes et al., 2002, 2007; Asl et al., 2020; Malekbala et al., 2017), enzymatic modification (Dikshit et al., 2020; Torres et al., 2011), deep eutectic solvents (Liu et al., 2019), among others researched in academia (Sherazi & Mahesar, 2016). On the other hand, this research is a pioneer in presenting results from a molecular distillation active process in the industry and is commercially viable.

2 Material and methods

2.1 Molecular distillation technology

The studied equipment is named "*De-acidification of fats and oils*" and it is split into four stages as shown in Figure 2 of patent number EP 2 597 142 A1 (Sarup, 2015).

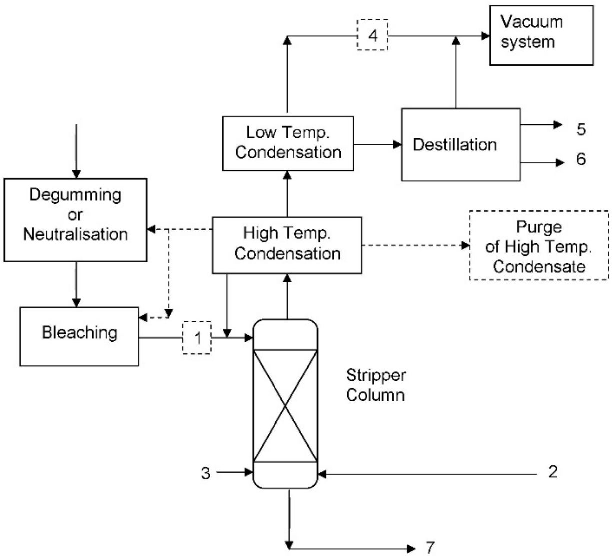

Figure 2. Patent Conception.

Step 1 (Deodorizer): a) the bleached oil stream (1) was fed to a vacuum stripping column with steam (2) and air leakage (3). In the vacuum stripping column (deodorizer), biocompounds, fatty acids, volatile gases and neutral oils were withdrawn and relocated to the next step 2 High Temperature Zone. The deodorizing equipment, in this research, was configured for 500 tons in 24 hours at 255 °C and 0.5 mbar. The step 1 equipment evaluated in this research pursued the methodology presented by De Greyt (2012) in Fig. 5 of his work.

Step 2 (High Temperature Zone): b) In that step, neutral oils were liquidized from the vapor stage. The condensed neutral oils were kept and sent back directly to the stripping column or indirectly to a bleaching operation and/or for a degumming/neutralization operation. Other downstream of deodorized oil was set on 7 line. This equipment operated with 0.5 mbar, 197 °C and a capacity of 12.5 tons/day.

Step 3 (Low Temperature Zone): c) volatile fatty acids, biocomponents and other volatiles passed to a cold condensing zone. In that cold chamber, volatile fatty acids, microelements along and other volatiles were liquefied (SODD). A four-stream flow compounded of non-condensable gases and other lighter molecules went through the vacuum system. This equipment was operated with 0.5 mbar, 60 °C and capacity of 2.5 tons/day. The steps 3 and 4 encompass a unique equipment methodology presented by De Greyt (2013) in the Figure 5 of his work.

Step 4 (Tocoboost molecular distiller): d) the condensate (SODD) of volatile fatty acids, micronutrients along with other volatiles ones was transferred to a distillation section to separate the condensate into a fatty acid enriched product 5 steam (fatty acid steam), a residual 4 steam (vacuum) and micronutrients 6 (tocopherol steam) enriched flow. Tocoboost was configured according to the following average parameters: inlet flow at 1,250kg/hour; concentrated tocopherol recirculation flow rate distillate at 30 kg/hour; distillate inlet temperature at 150 °C; Tocoboost outlet temperature at 224 °C; inlet vacuum at 1.34 mbar and outlet vacuum at 1.2 mbar. The step 4 equipment methodology surveyed in this research was the same presented by Díaz-Tovar et al. (2011) in the Figure 1 of his work.

2.2 System sampling

The distillate samples were collected in step four, at the three points of the system (initial distillate, concentrated fatty acid distillate and concentrated tocopherol distillate), always between 8 and 9 am from July/2019 to February/2020, in 250 ml amber polyethylene bottles, Nalgon brand, model No. 2320 and refrigerated at 0 °C until the moment of analysis, totalizing 81 days. Analyzes were performed within 72 hours after sample collection. The samples were stored at 4 °C until the day of analysis.

2.3 Analysis

For analysis, it was used an Agilent brand Gas Chromatograph (GC) equipped with Flame Ionization Detector (FID), Agilent DB-5HT column (30 mx 0.25 mm x 0.1 µm) and Helium carrier gas with approximately 2 mL/min according to official methods AOCS Ce 3.74 and AOCS Ce 7-87. In addition to the daily samples, it was carried out sample readings of 5% and 20% known values of tocopherol standards. The reagents used in the methods were as following: Pyridine (CAS #110-86-1); BSTFA + 1% TMCS, Toluene (CAS #108-88-3); Heptadecanyl stearate (HDS); Glicerol (CAS #56-81-5); Methyl stearate (CAS #112-61-8); Á???(CAS estee #11 (CAS #57-11-4); 1-stearoyl-rac-glycerol (CAS#123-94-4); α-Tocopherol (CAS #10191-41-0); Stigmasterol (CAS #83-48-7); Cholesteryl Stearate (CAS #35602-69-8) and Glyceryl Tristearate (CAS #555-43-1) of analytical grade purchased from HEXIS, Sao Paulo, Brazil.

2.4 Sample material

The SODD used in the research was produced in refineries that have a physical soy oil refining process in the stage of crude degumming soy oil with PLA (phospholipase A) enzymes of the *Aspegillus Niger* type from the Novozymes company, 25 ppm per ton. The SODD was extracted from soybean oil from intacta 1, cultivar with genetic technology, in order to protect it against *Agrobacterium tumefaciens* and *Bacillus thuringiensis* pests. A picture of the product samples is presented in Figure 3.

Figure 3. Product Samples, From the left to the right: 1 - Refined soybean oil from Step 1 (deodorizer); 2 – SODD from Step 3 (Low Temperature Zone) - stream; 3 - SODD from Step 4 (Tocoboost molecular distiller) – enriched fatty acid stream; 4 – SODD from Step 4 (Tocoboost molecular distiller) – enriched tocopherol stream.

2.5 Tocopherol recovery, concentration and degradation

Tocopherol's recovery and concentration method of calculation at the Tocoboost equipment was done by mass balance flow rate. The formula used was ([Inbound SODD flow rate * Tocopherol concentration] - [Outbound SODD flow rate (FFA Concentrate) * Tocopherol concentration] - [Outbound SODD flow rate (Tocopherol Concentrate) * Tocopherol concentration]) / [Inbound SODD flow rate * Tocopherol concentration]). The loss of tocopherol in both SODD outbound flow rate was regarded as tocopherol degradation.

3 Results

Table 1 shows the average results of the tocopherol and fatty acid concentrations evaluated. Due to commercial and laboratory demands the product is not evaluated every day. The days were selected where the three SODD streams, one input and two outputs of the processes, were fully evaluated totalizing 81 days within an 8-month period.

Table 1. Average results.

Distillate	Flow rate kg/Hour	Tocopherol %	Free Fatty Acids %	Mono acyl glycerides %	Diacyl glycerides %	Triacyl glycerides %	Steryl esters %	Squalene %	Sterols %
SODD Inlet Stream	1,244.83	2.9971	76.6102	0.8333	0.8763	0.9446	1.3448	0.5481	1.6899
Fatty acid output concentrated stream	1,039.14	0.0984	89.4235	0.1338	0.1065	0.2752	0.3300	0.1596	0.0729
Tocopherol output concentrated stream	208.54	15.7929	15.7999	1.1421	5.9480	15.5977	14.4787	2.6027	4.6054

The results for the entire analyzed period are presented in the Supplementary Material in Tables S1, S2 and S3.

Considering all the evaluated factors, it is possible to infer that the distillate production average flow was 1,244.84 kg/h (input stream), 1,039.14 kg/h (fatty acid stream) and 208.54 kg/h (tocopherol stream). The concentrator inlet temperature presented an average of 149.63 °C +/-1.85, column temperature of 224.56 °C +/-1.62 and 1.34 mbar +/-0.34 vacuum average. The tocopherol content average was 2.9971% for the input SODD and 15.79% for the resulting concentrated distillate stream, which corresponds to 5.28 of the concentration capacity. The fatty acid average content was 76.6125% for the inlet distillate (raw material) and 89.4235% for the concentrated distillate stream, 1.16 times the inlet SODD. The flow, temperature and vacuum were measured by transmitters installed in the equipment and it is reported in Supplementary Material Table S4. All others values refer to the results of chromatography analysis.

4 Discussion

4.1 Multiple stages of backset distillation.

The equipment evaluated has a set of 5 shorts path ascending clean film evaporators that work in continuous flow and counter current flow in 2 closed circuits and the concept is close to the one presented by Laoretani & Iribarren (2018), for structure optimization of the multistage molecular distillation recycling process. The scheme presented has two molecular distillation stages for the separation of FFA into SODD and to obtain tocopherol concentrate in the residual stream, within the acidity specifications with backset flow. By using multiple counter flow distillation stages, the equipment obtains a very high concentration performance on an industrial scale.

4.2 Temperature

Temperature is a key important factor regarding tocopherol concentration in SODD. Sarup (2015) in his article on advances and challenges in lipid processing modeling, presented a lipid distillation modeling in double scrubber equipment from Alfa Laval company, which could improve tocopherol concentration and yield with 170 °C of temperature, in the de-acidification of soybean oil.

As in molecular distillation, the initial product will always be divided into two streams, which the Tocoboost equipment has two distillation chambers: A chamber to distill the concentrated tocopherol SODD stream in a closed counter flow circuit, which operated at 150 °C inlet temperature; and a second chamber above it, which operated at 224 °C to distill the concentrated fatty acid SODD stream.

Using a falling film evaporator under 0.1Pa pressure, 160 °C evaporation temperature and feed rate of 10.4 g min^{-1}, Altuntas et al. (2018) reduced the amount of FFA from 57.8% to 6.4% and increased tocopherols concentration from 8.97% to 18.3%, which is equivalent to 81.23% of the tocopherol recovery in hazelnut oil. This study demonstrated that tocopherol recovery was better at temperatures below 180 °C and that higher temperature and vacuum values achieved better de-acidification in the residual oil stream.

The effects of evaporation temperature, discharge rate and wiper roll speed (vacuum) on the tocopherol yield in the canola oil deodorizing distillate were evaluated (Jiang et al., 2016) and using a feed rate of 90 mL h^{-1} and 200 °C temperature, the tocopherol content was recovered (almost 35%) in the vapor phase (distilled). However, by raising the temperature to 230 °C, part of the phytosterols and MAG started to be retrieved also in the steam stage and this activity reduced tocopherol concentration.

Ketenoglu et al. (2018) experimented molecular olive pomace oil distillation in order to separate tocopherol from squalene and the best condition, among 20 tested variations, was 160 °C and 0.072 mbar aiming to obtain the highest tocopherol concentration, demonstrating that a lower temperature and higher vacuum is ideal for distilling this component in the evaluated product.

Yeoh et al. (2014) reported that the distillation/separation occurs in the following order: MAG < DAG < TAG due to the specific glyceride sequence length and steam pressure of different acylglycerols. They found out that the TAG was totally removed from acylglycerol compound at the elevated temperature of 250 °C and that the DAG distillate purity was 54.4% by weight. The second step of the short path molecular distillation involved FFA removal and MAG at the lower evaporator temperature of 180 °C, yielding the final concentrated DAG oil in the residue with 89.9% by weight purity. This result is notably important to comprehend the performance and concentration capacity of the Tocoboost equipment, because as MAG, due to its molecular weight, it has an ideal distillation temperature close to the tocopherol. MAG component has a statistical correction with a positive effect on tocopherol concentration in the SODD, by separating the tocopherol concentration circuits in the chamber with a lower temperature, and the concentration of DAG and TAG in the chamber/zone with a temperature above 200 °C, Alfa Laval modeled the equipment for high performance.

According to Díaz-Tovar et al. (2011), condensation zones are carried out as washing operations, where the condensed liquid is recirculated in a packaged section (shown in photo 3) to remove the condensable volatiles from the steam.

Regarding the double scrubber, the equipment that is part of the patented technology is installed right after the deodorizer operation. The high condensing chamber works between 160 °C to 210 °C, and the low zone is operated between 50 °C to 75 °C. It is important to point out in this research the development of a huge lipid compounds database, as well as data about molecular structures and physical properties that allowed us to understand the equipment operation. Thus, after comparing the results of experiments carried out in simulators at universities with the results obtained in the Tocoboost equipment in operation, it is possible to infer that chambers operated at low temperatures in the double scrubber and tocoboost are important steps to concentrate the tocopherol in the obtained quantity in this research.

4.3 Vacuum

The recorded value in the equipment's meters was an average of 1.34mbar for the inlet vacuum (in the equipment lower part) and 1.2mbar for the outlet vacuum (upper outlet for the vacuum system).

Using the differential scanning calorimetry technique, Damaceno et al. (2014) found out that the α-, β-, δ- and γ-tocopherol boiling point value at vacuum was 1.1 kPa. The registered value in the operation of the patented equipment, (0.134 kPa) was lower than that registered in the research (1.1 kPa), and this allowed changing the tocopherol boiling point to a temperature lower than that registered in the research, which was around 275 °C. This is one of the reasons why the equipment has a recovery rate greater than 5x the tocopherol concentration in the input SODD, it works in a higher vacuum range and lower temperature, which allows for reducing tocopherol degradation in the DM process.

In a SODD molecular distillation research, Hirota et al. (2003) found that at 0.026 mbar, FFA, MAG, tocopherols and sterols were concentrated in the distilled fraction, due to the boiling points of these compounds being lower than 600 g mol^{-1}. On the other hand, DAG, TAG and sterile esters were concentrated in the residue fraction due to their components having a molecular weight greater than 600 g/mol at 0.026 mbar. In the patented equipment, it was identified that a greater amount of TAG and sterile esters, in the input SODD, under the evaluated temperature and vacuum, had a negative effect on the tocopherol concentration.

4.4 Recovery and concentration

In this evaluated patented technology, the tocopherol content average result was 2.9971% for the input SODD and 15.79% for the concentrated distillate resulting stream, which corresponds to 5.28 times the concentration and recovery capacity was 100% of the initial distillate.

In their research, Martins et al. (2006) reported that 160 °C evaporator temperature and 10.4 g min^{-1} feed flow was the best molecular distillation condition to obtain the best concentration and tocopherol recovery in SODD, reducing exposure to infinitesimal oxygen, light and high temperature, that one may prevent its decomposition. Martins achieved a concentration of 18.3% (more than twice the initial stream concentration) and 99.6% recovery.

4.5 Tocopherol degradation

In the patented equipment tocopherol degradation was 9% $\pm$ 0.08%. As the equipment is hermetic, tocopherol losses can occur due to an increase in the evaporated product in the distillation chamber due to an increase in temperature. Posada et al. (2005) reported that some tocotrienols contents are invariably lost during molecular distillation. However, it is known that these components are not expected to decompose or oxidize in this extraction condition and in their research, Tocotrienol losses of less than 20% were recorded during the distillation tests. Kmiecik et al. (2019) verified that the exposure of canola oil to a temperature of 170 °C and the presence of oxygen for 6, 12 and 18 hours, in their research about tocopherol molecules degradation and its impact on the polymerization of triacylglycerols during the heat treatment of oil and it was found a drastic reduction in the tocopherol amount in the final product.

4.6 Input product quality variations

During the evaluated period, there were no changes in the molecular distillation equipment setup. Vacuum, temperature, flow and other operating variables were constant, but there is no control over the raw material (SODD sent by suppliers). When suppliers have changed their processes, the received product might present different concentrations. The plant may also receive chemical refining products that have a distinct characteristic from physical refining plants. An example of this situation occurred on 08/31/2019, SODD (29,940kg) of the DVT8949 vehicle is shown in Table S5 in the Supplementary Material.

This product was put into the system and then mixed with the product that has already been in the tank. On 09/06/2019, it was performed an analysis and the results are shown in Supplementary Material Table S6, comprising the data about the SODD of the input stream of the concentrator, tocopherol content of 4.05%, fatty acid of 57.77% and other components changed to the expected variability.

The output stream SODD results of concentrated tocopherol on days 6, 10 and 11/09/2019 are shown in the Supplementary Material Table S7, thus presenting lower tocopherol concentration content than the expected average.

4.6.1 Neutral oil losses reduction

The situation mentioned above is explained by Gunawan & Ju (2009). They could state that TAG, DAG and MAG (acylglycerols) are also known as neutral oil. SODD from chemical refining sources contains a higher level of acylglycerols (around 10% to 20%) than physical refining (8%). TAG are neutral oil's main components. The vehicle above had the SODD with 19% of total neutral oil content and after being stored in the tank, it raised to 4%. Lima & Sarup et al. (2013) informed that the patented equipment distills SODD with a minimal amount of neutral oil and fatty acid (FFA) practically absent from DAG and TAG, presenting only MAG traces.

4.6.2 Diacylglycerols migration

In their research, Xu et al. (2001) evaluated the acylglycerols migration effects on the medium fraction of palm oil through molecular distillation and found out that the higher temperature plus prolonged time increased the extent of oil migration neutral, while the FFA content in the product decreased. It was also observed that DAG had a significant effect on the distribution of the fatty acids in TAGs because DAG can be faster transformed into triacylglycerols than MAG during high temperature distillation. Temperature above 200 °C caused significant migration of DAG according to Compton et al. (2008).

The increase in the level of DAG in the SODD (Lima & Sarup, 2013) tends to difficult tocopherol concentration because of micronutrient loss in the evaporation of the neutral oil. Yeoh et al. (2014), while conducting their research on DAG in enriched palm oleins, found out that the higher evaporator temperature of 250 °C in the first step induced a representative migration of acylglycerols and, consequently, the unstable isomers DAG conversion on both undesirable, TAG and MAG products. Solaesa et al. (2016) found an ideal temperature of 155 °C for the MAG distillation on sardine oil, closer to the temperature used in the inlet SODD of the patented equipment lower chamber.

In their research simulating continuous physical refiners for de-acidifying palm and coconut oils, Ceriani & Meirelles (2006) identified that at higher temperatures, the volatility of DAG and MAG increased and these compounds were vaporized from the oil, increasing neutral oil content loss as a mechanism of two distinct contributions: acylglycerols vaporization (mainly DAG and MAG, which are more volatile than TAG); and mechanical transport of liquid oil droplets, mainly composed of TAG. With a greater amount of acylglycerols (neutral oil) in the system, the patented equipment was configured, concentrating a smaller amount of tocopherol in the output stream.

The physical refining process in this patented technology must be carried out through the use of the phospholipase A (PLA) enzyme. The enzyme promotes higher refining yields by alchemizing phospholipids into DAG. Nevertheless, the augment of DAG in oils leads to boost neutral oils losses problem at the deodorization step by concentrating it into the SODD (Ceriani & Meirelles, 2006; Yeoh et al., 2014; Xu et al., 2001). However, as the patented set has a "double scrubber" the SODD stream, which is rich in neutral oil, goes back to the system and the SODD stream rich in tocopherol goes to the upper zone of the equipment and condenses at a temperature around 55 °C. In this way, both neutral oil loss mechanisms are eliminated. This allows the production of an initial SODD (after deodorizer and double scrubber) presenting minimal neutral oil amount.

4.7 Correlation between micronutrients and tocopherol

Over 1900 results were evaluated from 243 analyzed samples, specifically in the patent set, it was possible to statistically evaluate through regression in Minitab software, linear correlation (Pearson), positive or negative effect between the input stream SODD components and its relationship to tocopherol concentration results in the equipment output stream. Table S8 (in the Supplementary Material) presents the results and the impact on tocopherol concentration separately.

For all results where "Pearson" correlation obtained a result close to 50% and statistical significance "*p*- value" $p < 0.05$, a regression equation was created which will be presented in Table S9 (in the Supplementary Material).

Multivariate regression of the 5 components above the SODD input was performed and it was found a correlation of 73.00% and $p < 0.001$ with tocopherol concentration in the final distillate, as shown in Figure S4 (Supplementary Material). The two most relevant components for the multivariate regression results were tocopherol percentage (positive) and TAG (negative) in the input SODD. Steryl ester had no impact when added along with the other four ones in the model, as shown in Figure S5 (Supplementary Material). The Final equation was defined as: %Tocopherol = 0.1257+1.075X1 + 0.01247X2 + 0.00393X3 – 0.01107X4 – 0.00241X4^2 + 0.549X1*X4 – 0.02128X2*X3. Ceriani et al. (2013) performed the steam prediction and found the boiling points for the molecules containing the concentrated tocopherol SODD and this work clarifies the mathematical equation found in this list of patented equipment. Micronutrients that have a boiling point close to tocopherol had a positive correlation, while those that were distant, presented a negative relationship.

5 Conclusions

When evaluating tocopherol industrial scale in molecular distillation equipment, it was possible to infer that it is possible to achieve over five times Vitamin E concentration from non-modified soybean oil deodorizer distillate in a physic enzymatic phospholipase degumming process plant using a combination of advanced technology to the separation of high value-added molecules gained through studied hypotheses regarding vacuum, temperature, distillers models, backset flows, multiple stages of distillation, degradation and product recovery.

The combination of factors mentioned above resulted in a statistical multivariate correlation from output concentrated distillate flow with the inlet raw material micronutrients.

New researches need to be carried out to evaluate tocopherol concentration on an industrial scale using as raw material a SODD from a chemical refining process or chemically modified.

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Supplementary Material

Supplementary material accompanies this paper.

Table S1. Industrial production research period.

Table S2. Output stream results.

Table S3. Output stream results.

Table S4. Result data of process variables and tocopherol degradation.

Table S5. DDOS analysis results – Vehicle DVT8949.

Table S6. DDOS analysis results – Tank.

Table S7. Output Tocopherol concentrated regarding DDOS analysis results.

Table S8. Statistical correction of factors.

Table S9. Regression equations.

Figure S4: Minitab Multivariate Regression.

Figure S5: Main Impacting Components.

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