

Green cosmetics via bio-oil

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ABSTRACT

The refining of crude vegetable oil results in an unused sidestream, the oil deodorizer distillate (ODD). This distillate contains valuable ‘minors’, like squalene, tocopherols and sterols, which have applications in the cosmetic, pharmaceutical and nutrition industry. Therefore, their successful separation from this sidestream increases the viability of a refinery. The separation is achieved by supercritical esterification and supercritical CO₂ extraction. The objective of this study is to simulate the process with Aspen[®] and model the kinetics with AVS[®]. Different ODD are investigated with HT soybean giving the highest yield. Additionally, an economic analysis is performed to estimate the process profitability.

Keywords

Oil deodorizer distillate, supercritical, esterification, extraction, squalene, tocopherols, sterols, green cosmetics

INTRODUCTION

To produce edible vegetable oils, a refining process of the crude oil is needed to remove any undesirable components such as free fatty acids, pigments, gums, waxes etc. During the refining, a side stream containing oil deodorizer distillate (ODD) is created. This stream consists mainly of free fatty acids (FFA’s), glycerides and ‘minor components’, such as squalene, tocopherols and sterols, and is currently considered a waste product. It has, however, great valorization potential since the minor components have important applications in the cosmetics, pharmaceutical and nutrition industry [1, 2, 3]. Presently, squalene is typically obtained by extraction from shark livers. The oil deodorizer distillate could present a much desired sustainable source for squalene if it could be separated from the ODD stream. A possible separation process comprises a supercritical esterification with ethanol followed by a supercritical extraction with CO₂. The esterification unit was already designed and dimensioned in a previous project. In this project, the sensitivity of the unit to the ODD composition and alcohol composition was studied. The extraction unit however still needs to be designed and dimensioned.

The goal of the esterification is the conversion of the FFA’s in the ODD to fatty acid ethyl esters (FAEE). This step is done in order to increase its solubility difference compared to the ‘minor components’. Due to this modification, the isolation of the ‘minor components’ by supercritical extraction with CO₂ becomes possible. By working under supercritical conditions, triglycerides and ethanol become completely miscible. This improves the esterification rate and allows for a continuous process [4, 5].

Supercritical CO₂ has a low viscosity, low surface tension and high diffusivity, which makes it extremely useful as an extraction solvent. Moreover it is inert and non-toxic

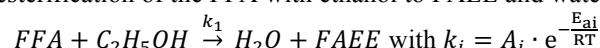
which is important for further processing in the nutrition industry.

MODELLING THE SUPERCRITICAL ESTERIFICATION

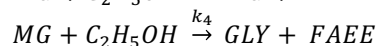
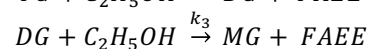
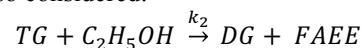
Athena Visual Studio[®] is a software package used to model the kinetics of chemical reactions. The unknown kinetic parameters in the Arrhenius equation are estimated through residual sum of squares minimization using experimental data.

Experimental data

The experimental data of the esterification, necessary for modelling the kinetics, are provided by VITO. 36 experiments with sunflower ODD were performed in a plug flow reactor. The reaction investigated is the esterification of the FFA with ethanol to FAEE and water.



The stepwise reaction of the triglycerides (TG) with the ethanol to form glycerol (GLY) and the corresponding FAEE is also considered:



Here, DG refers to diglyceride and MG to monoglyceride. The pressure is held at 15.0 MPa, and the ethanol to ODD ratio is 0.6 g g⁻¹. The experiments are carried out at three different temperatures: 523 K, 548 K and 573 K. At several residence times, samples are taken and analysed via GC-analysis to determine the product stream composition.

Determination of the kinetic parameters

In this model, all reactions are considered to be elementary and reversible. The estimated Arrhenius parameters through regression of the kinetic model to the experimental data can be found in Table 1. Here, the subscript refers to the reaction. The plus and minus in superscript refer to respectively the forward and backward reaction. The estimated values show a fairly decent correspondence to those found in literature [6, 7]. Two parameters, however, are not significantly estimated which can possibly be attributed to the corresponding steps being quasi-equilibrated.

Table 1. Kinetic parameters estimated by Athena Visual Studio[®].

| estimated value [m ³ s ⁻¹ mol ⁻¹] | | estimated value [kJ mol ⁻¹] | |
|--|---|--|-------------|
| A ₁ ⁺ | 4.14 10 ⁻⁷ ± 1.27 10 ⁻⁷ | E _{a1} ⁺ | 55.9 ± 43.2 |
| A ₁ ⁻ | 3.19 10 ⁻⁵ ± 2.83 10 ⁻⁶ | E _{a1} ⁻ | 19.5 ± 16.0 |
| A ₂ ⁺ | 7.58 10 ⁻⁷ ± 1.63 10 ⁻⁷ | E _{a2} ⁺ | 44.9 ± 31.6 |
| A ₂ ⁻ | 2.61 10 ⁻⁵ ± 4.76 10 ⁻⁶ | E _{a2} ⁻ | 39.6 ± 32.2 |
| A ₃ ⁺ | 6.36 10 ⁻⁷ ± 1.07 10 ⁻⁷ | E _{a3} ⁺ | 96.9 (n.s.) |
| A ₃ ⁻ | 2.80 10 ⁻⁵ ± 1.64 10 ⁻⁵ | E _{a3} ⁻ | 43.3 ± 41.0 |
| A ₄ ⁺ | 4.79 10 ⁻⁶ ± 2.2 10 ⁻⁶ | E _{a4} ⁺ | 107 (n.s.) |
| A ₄ ⁻ | 2.53 10 ⁻⁵ ± 9.18 10 ⁻⁶ | E _{a4} ⁻ | 134 ± 69.9 |

In Figure 1 and Figure 2, the experimental and simulated yields are plotted as a function of the residence time for a temperature of respectively 523 K and 548 K. The yield of the FAEE is underestimated, while the yield of the FFA is overestimated. The difficulties in describing the yield are due to the fact that two of the activation energies weren't estimated significantly. However, the trend of the simulations seems to be correct. The components participating in the esterification reaction of the FFA are modelled rather well, while there is room for improvement concerning the diglycerides and monoglycerides. These intermediate components are modelled rather poorly, attributed to the very small quantities in which they are present.

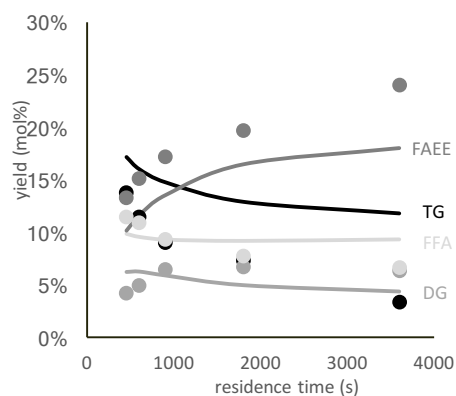


Figure 1. Comparison of the experimental yield (dots) to the result of the non-isothermal regression (full line) of TG (black), DG (second lightest grey), FFA (lightest grey) and FAEE (darkest grey) at 523 K, 15.0 MPa and ethanol/ODD ratio of 0.6 g g^{-1} .

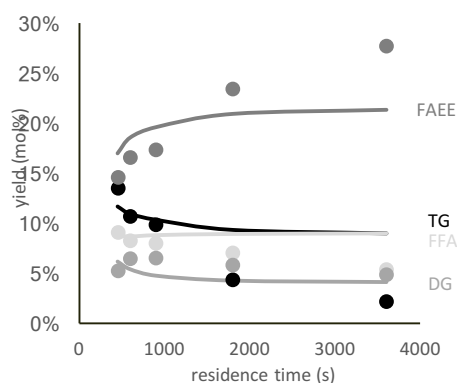


Figure 2. Comparison of the experimental yield (dots) to the result of the non-isothermal regression (full line) of TG (black), DG (second lightest grey), FFA (lightest grey) and FAEE (darkest grey) at 548 K, 15.0 MPa and ethanol/ODD ratio of 0.6 g g^{-1} .

SIMULATION OF THE ESTERIFICATION UNIT

Aspen Plus[®] is a software package which allows the design, modelling and optimization of a chemical process.

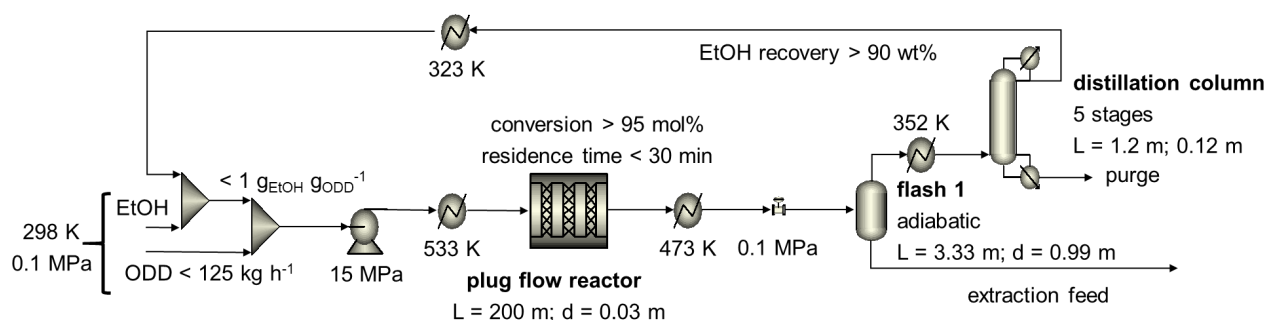


Figure 3. Process configuration of the esterification.

Based on the laws of conservation of mass and energy, equilibrium relations and reaction rate correlations, the software is capable of predicting the behaviour of a completely integrated process.

Process configuration

The process configuration for the esterification, including the criteria imposed by the industrial partners, is represented in Figure 3. The chemical kinetics as found in literature [6, 7] are implemented in this process scheme. The configuration is originally designed to meet the criteria with a feed mixture containing ethanol and ODD originating from the refining of sunflower oil. In the second mixer, the ODD is mixed with the total ethanol stream. Before the mixture is introduced in the reactor, the pressure and temperature are augmented to the maximum allowed values of respectively 15.0 MPa and 553 K to obtain the highest possible conversion. The resulting stream is then fed in the tubular reactor, where the esterification takes place. The dimensions of the reactor correspond to the already existing one at Indinox. Inevitably, several side reactions occur, such as the stepwise reaction of triglyceride with ethanol resulting in glycerol. After reaction, the stream is cooled to 473 K and the pressure is reduced to 0.1 MPa. The stream is then sent to a flash, which separates the water and ethanol from the product stream. The minor components, together with the esters, the unreacted free fatty acids and glycerides make up the bottom fraction. This stream will therefore be the feed for the extraction. The top fraction consists mainly of water and ethanol and is brought to a temperature of 352 K, which is right above the boiling point of ethanol, but below the one of water. Therefore the bottom fraction of the distillation column will mainly consist of water, which is purged. The top fraction however will be mostly ethanol, which is recovered and mixed with fresh ethanol to form the total ethanol stream.

Influence of the ethanol composition

Less concentrated ethanol mixtures are economically more interesting. Therefore, it is interesting to study the influence of the ethanol concentration on the yield of minor components. Three different compositions are tested, being azeotrope ethanol, technical grade ethanol and bio-ethanol. The exact compositions of the mixtures can be found in Table 2.

Table 2. Compositions in wt% of the different ethanol mixtures.

| | azeotrope | technical grade | bio |
|-------------|-----------|-----------------|------|
| ethanol | 95.6 | 60.0 | 75.9 |
| water | 4.4 | 30.0 | 24.1 |
| methanol | 0.0 | 5.0 | 0.0 |
| isopropanol | 0.0 | 5.0 | 0.0 |

The results of the simulations for the bottom stream of the flash, which is the feed for the extraction, is shown in Table 3. When comparing the effect of the ethanol composition, it should be noted that the relative amount of minor components in the product stream is more or less the same (± 13 wt%) for the three ethanol compositions. However, an increase in the absolute yield is noticed with increasing concentration of the ethanol mixture. This can be explained by the observation that the distillation column is the bottleneck of the process. One of the imposed criteria is to obtain a recovery of 90 wt% ethanol with a certain purity. Less concentrated ethanol mixtures contain more water and therefore require more refluxing to meet the criterium. Only one distillation column will be built, so the capacity of the column is constant for the three cases. More incoming reflux therefore implies a smaller inlet in the column. This can only be achieved by an overall smaller flow, which implies that fewer minor components enter the system and therefore a lower yield of minor components is obtained. In conclusion, the highest yield is obtained with the purest mixture, i.e. azeotrope ethanol.

Table 3. Mass flow of the feed for the extraction in kg h^{-1} .

| | azeotrope | technical grade | bio |
|------------------|-----------|-----------------|------|
| minor components | 22.8 | 13.3 | 16.1 |
| FAEE | 73.4 | 43.1 | 52.3 |
| glycerides | 30.2 | 17.5 | 21.2 |
| other | 27.7 | 28.7 | 37.4 |

Comparison with soybean oil deodorizer distillate

The question arises whether the process configuration, which is designed for sunflower ODD, can be used with a feed of ODD originating from other vegetable oils. Two different kinds of soybean ODD are tested, being ‘high tocopherol’ (HT) and ‘low tocopherol’ (LT) soybean ODD. The compositions of the distillates are represented in Table 4.

Table 4. Composition in wt% of ODD from sunflower, HT soybean and LT soybean oil, as produced by Cargill.

| | sun-flower | HT soy | LT soy |
|------------------|------------|--------|--------|
| minor components | 18.3 | 63.9 | 2.0 |
| FFA | 56.0 | 20.4 | 90.2 |
| glycerides | 24.2 | 13.6 | 1.7 |
| FAME | 1.5 | 2.0 | 6.1 |

The simulation results suggest that the design criteria can be met with the same process configuration. The highest yield in minor components in the product stream of the esterification, which will be the feed for the extraction, is obtained with a feed of high tocopherol soybean ODD

(see Table 5). This shouldn’t be too surprising, since this distillate initially already contained the highest fraction of minor components. The use of low tocopherol soybean oil deodorizer distillate results in the lowest yield.

Table 5. Mass flow of the feed for the extraction in kg h^{-1} .

| | sun-flower | HT soy | LT soy |
|------------------|------------|--------|--------|
| minor components | 22.8 | 79.9 | 2.1 |
| FAEE | 73.4 | 27.5 | 97.5 |
| glycerides | 30.2 | 17.0 | 6.2 |
| other | 27.7 | 13.5 | 29.4 |

SIMULATION OF THE EXTRACTION UNIT

After the esterification, a supercritical extraction with CO_2 is carried out to isolate the minor components. The extraction unit is also simulated using Aspen Plus[®].

Process configuration

The process configuration for the esterification, including the criteria imposed by the industrial partners, is represented in Figure 4. Fresh CO_2 (10 l h^{-1}) is mixed with recycled CO_2 and then sent to a compressor. In 3 stages and with intercooling, the CO_2 is brought to a pressure of 10.0 MPa and a temperature of 313 K. At these conditions, the CO_2 is supercritical and displays all the advantages as mentioned in the introduction. 2 l h^{-1} of the bottom fraction of the flash in the esterification unit forms the feed for the extraction, after also being brought to a pressure of 10.0 MPa by a pump. The feed and the CO_2 are subsequently brought together in the extraction column. The feed flows from the top to the bottom of the column, while the CO_2 streams upwards. Separation is achieved based on the difference in solubility in CO_2 of the different components in the feed. Components that dissolve well in CO_2 , will end up in the top fraction (extract), while the other components will make up the bottom fraction (raffinate). The pressure and temperature of the extract are then lowered to respectively 0.1 MPa and 298 K, to separate the CO_2 from the ‘minor concentrate’ in a flash (F1). Some of the CO_2 is recycled and, as mentioned before, mixed with fresh CO_2 . However, a fraction of the CO_2 is purged to avoid accumulation in the process. The raffinate is also further separated in a flash (F2) at a pressure of 0.1 MPa and a temperature of 633 K. These conditions will lead to a top fraction of fatty acid esters in the gas phase and a bottom fraction of sterols in the liquid phase.

Dimensioning of the equipment

An important aspect of a model is the dimensioning of the equipment, i.e. determining the diameter and height. The extraction column is dimensioned according to the theoretical plate method [8]. An internal diameter of 0.15 m and a height of 1.5 m is found.

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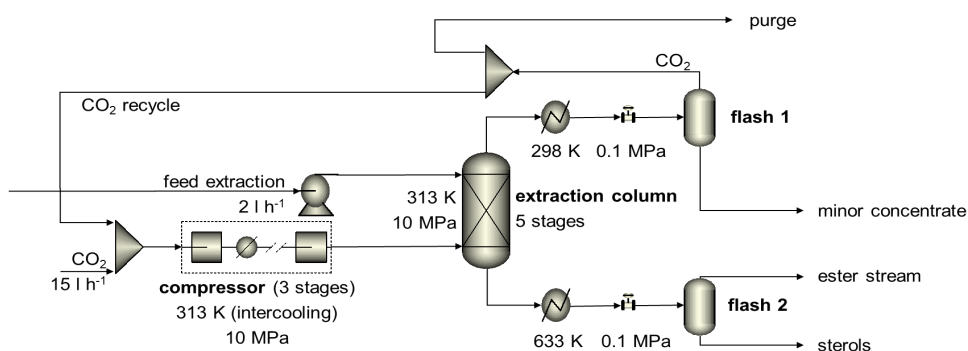


Figure 4. Process configuration of the extraction.

Calculations show flash F1 (used for separating the extract) should have a diameter of 0.28 m and a height of 1.60 m, while flash F2 (used for separating the raffinate) should have a diameter of 0.03 m and a height of 0.20 m [9]. The dimensions of flash F2 seem very small, but this is due to the low incoming flux (1.2 kg h^{-1}).

Results

The extraction is carried out with an initial feed of sunflower ODD and azeotrope ethanol. There are three important product streams: the minor concentrate, a fatty acid esters stream and a sterols stream. The results of the simulation are shown in Table 6.

Table 6. Mass flow in g h^{-1} of the product streams of the extraction.

| | minor concentrate | fatty acid esters stream | sterols stream |
|-------------|-------------------|--------------------------|----------------|
| tocopherols | 45 | 0 | 0 |
| squalene | 34 | 0 | 0 |
| sterols | 0 | 0 | 130 |
| FAEE | 0 | 672 | 0 |
| FAME | 0 | 18 | 0 |
| glycerides | 61 | 216 | 0 |
| other | 3 | 181 | 1 |

The sterols stream has a purity of over 99 wt%. The fatty acid ester stream consists mainly of FAEE, but also contains some other components like ethanol, FFA, glycerides and water. This stream can be further processed into biodiesel. The tocopherols and squalene are found in the minor concentrate, but require further separation. A sequence of flashes, a distillation column as well as an extraction column were all tested, but seemed ineffective. This is due to the unavailability of interaction coefficients between the minor components and the glycerides.

It should be noted that the yield is rather low (a minor concentrate of 0.14 kg h^{-1} and a sterols stream of 0.13 kg h^{-1}). However, this is due to the low influx of feed in the extraction column. An evident method to increase the yield, is to increase the current influx of 2 l h^{-1} feed and $10 \text{ l h}^{-1} \text{ CO}_2$. Upscaling also implies redimensioning the extraction column and the flashes.

ECONOMIC ANALYSIS

Beside the technical part, there is also the economic aspect of the process which might be more important to raise the interest of companies and investors.

First, the added value of the process was calculated. This was done by determining the sale price and yield of each valuable component formed in the process minus the price of the input streams (alcohol and oil deodorizer distillate). It was assumed that the output stream from the esterification can be separated into the pure components and by-products like water and glycerol were not taken into account. A maximum added value of M€ 13.1 per year was found for the combination of azeotrope ethanol and sunflower oil deodorizer distillate. Maximum values were observed using HT soybean oil deodorizer distillates with an added value reaching M€ 30.8 per year for the combination with azeotrope ethanol. When this process will be carried out the price of ODD can raise enormously because it isn't a waste stream anymore. This and a non-complete separation could lead to a decrease of the profitability.

The capital cost was estimated using the method of

Guthrie and was only carried out for the process setup of the esterification. As the output of the extraction (i.e. the minor concentrate and sterols stream) is still very low, upscaling is required, which makes calculations for the current setup useless. The calculated capital cost is k€ 150 which is not much compared to the added value. This is mainly because the setup is rather small and it's only one part of the process.

Ultimately the energy cost for the esterification was calculated. On the one hand there is electricity required to compress the stream to 15.0 MPa with a centrifugal pump. On the other hand steam is needed to warm up the different streams. A PINCH analysis proved that it might be possible to recover some energy by linking heat exchangers. The total energy cost was computed to be k€ 15 per year (CO_2 -tax not included).

CONCLUSION

The oil deodorizer distillate can be a sustainable source of squalene, tocopherols and sterols which might be used in cosmetics, pharmaceutical and nutrition industry. A continuous process in which the 'minor components' are separated from the oil deodorizer distillates was investigated. The chosen path is to start with a supercritical esterification in which the free fatty acids are converted into free fatty acid esters. Then a supercritical extraction with CO_2 is carried out to separate the 'minor components' from the free fatty acid esters. Different compositions of alcohol were tested which all work for the chosen process setup. Also different kinds of oil deodorizer distillates were simulated. The process has potential to be a profitable process with an added value of € 13.1 million per year when starting from ethanol and sunflower oil deodorizer distillate.

ROLE OF THE STUDENT

The research of this report is part of the Cross-Course Project in the third year of the Bachelor of Science in Engineering: Chemical Technology and Materials Science at Ghent University. The topic was proposed by promoters prof. dr. ir. Joris W. Thybaut and prof. dr. ir. Jeriffa De Clercq. The research was performed under the supervision of ir. Alexandra Bouriakova. The execution of the simulations, the processing of the results as well formulation of the conclusions and the writing were equally divided between the five students.

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