An Intensified-Integrated Supercritical Extraction-Vacuum Distillation-Reactive Distillation Process to produce Phytosterols, Glycerol and Ultra-Clean Biodiesel from Crude Vegetable Oils

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Abstract

A novel intensified-integrated supercritical extraction (ScE)-vacuum distillation (VcD)-reactive distillation (RD) process to produce phytosterols (β-sitosterol and stigmasterol), glycerol and ultra-clean biodiesel from crude vegetable oils has been developed. The integrated process consists of two main sections: i) a supercritical extraction - vacuum distillation section, whereby using CO2 and a CO2-CH3OH mixture as supercritical fluids, the separation of triglycerides from phytosterols, phyto-glucoside compounds and fatty acids (FFA) is carried out. Further, the separation of phytosterols, phyto-glucoside compounds and the FFA by VcD is performed; ii) a second section where a RD column is used to perform the triglycerides transesterification reactions to produce ultra-clean biodiesel and glycerol. The effect of several operating conditions on the different process sections has been analysed. It was found that the operating pressure and the feed ratio of CO2/CH3OH mixture fed to the ScE column were the key variables to modify the phytosterols concentration produced in the first section. The methanol to triglyceride flow ratio in the RD section determines the complete conversion to produce a high-quality ultra-clean biodiesel.

**Keywords**: intensified-integrated process, phytosterols production, reactive distillation.

* 1. Introduction

Vegetable oils contain compounds in minor amounts that affect their quality and nutritional value, for example, phytosterols, tocopherols, waxes are some of the minor composition components in vegetable oils. Phytosterols are plant sterols that have structural and biological functions like cholesterol. They have been shown to have protective properties against various chronic diseases such as cardiovascular, hepatoprotective, diabetes and cancer. Regarding cancer prevention, it has been claimed that a diet rich in phytosterols can reduce the risk of cancer by 20% (Ju *et al*, 2004). Despite these health beneficial characteristics of phytosterols in the vegetable oils, these oils have been used to produce biofuels. Sterol glucosides (SGs) occur naturally in vegetable oils and fats in the acylated form. During the biodiesel conversion process, they are converted to nonacylated SGs. It has been found the presence of SGs in biodiesel, and it has been determined that these SGs contribute to flowability problems in biodiesel and biodiesel blends (Lee *et al*, 2007). Due to the high melting point of SGs and its insolubility in biodiesel or diesel fuel, SGs can essentially be considered "dispersed fine solid particles" in biodiesel. These dispersed SG particles may also promote the crystallization of other compounds. Therefore, a process to eliminate SGs in the production of biodiesel fuel and at the same time to produce the high health value phytosterols should be considered. The objective of the present work is to develop an intensified-integrated supercritical extraction (ScE)-vacuum distillation (VcD)-reactive distillation (RD) process to produce phytosterols (β-sitosterol and stigmasterol), glycerol and ultra-clean biodiesel from crude vegetable oils. Since CO2 is one of the most popular species to perform the extraction of valuable compounds from vegetable oils, the developed process in this work could be integrated with a CO2 capture process (Sofia et al., 2015) with environmental improvement.

* 1. Methodology

In order to develop the integrated-instensified process two aspects are considered: i) determination of the required thermodynamic properties and ii) the integration of the different sections of the process.

* + 1. Thermodynamic properties prediction of the complex mixture

To perform the simulation of the intensified-integrated process, a crude vegetable oil (Palm oil) with the following composition has been considered: triolein (0.488172 % wt.), tripalmitin (0.465289), oleic acid (0.044125), β-sitosterol (0.0004), stigmasterol (0.0001), α-tocopherol (0.001), β-carotene (0.0005), acylated β-sitosterol glucoside (0.00036), β-sitosterol glucoside (0.000055). Thus, the thermodynamic properties of the above mixture are required. Due to the lack of information about the thermodynamic properties of sterols and SGs compounds, it is necessary to use a group contribution method to calculate such properties. Figure 1(a) shows the generalized phytosterols molecule, where it can be observed that the radical (R) make the difference between cholesterol, β-sitosterol and stigmasterol. Figure 1 (b) shows the β-sitosterol glucoside molecule, where it is important to note the presence of OH and CH2OH radicals and oxygen bonds. With this molecule´s information, the thermodynamic properties were calculated using the computational tool ProPred (Constantinou and Gani, 1994). Due to space restriction, Table 1 only shows some of the predicted thermodynamic properties of β-sitosterol, stigmasterol and β-sitosterol glucoside. It should be noted that the values of the thermodynamic properties of sterols and β-sitosterol glucoside are quite different.



(b)

(a)

Figure 1. (a) Generalized phytosterol molecules and (b) β-sitosterol glucoside molecule

Table 1. Calculated thermodynamic properties using ProPred

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | Units | β-Sitosterol | Stigmasterol | β-Sitosterol-Glucoside |
| MW |  | 414.715 | 412.7 | 576.858 |
| *w* |  | 1.05429 | 1.0631 | 0.0913968 |
| Tb | K | 778.05 | 778.05 | 1456.81 |
| Pc | atm | 11.054 | 11.23 | 8.14 |
| Tc | K | 953.05 | 953.65 | 1977.11 |

* + 1. The intensified-integrated ScE-VcD-RD process

Figure 2 shows the optimal ScE-Vc flowsheet section obtained after intensive simulation to produce pure triglycerides at the bottom of the super critical extraction column and the separation of the phyto-sterols from the FFA at the vacuum distillation column. It was found that 30 equilibrium stages for the super critical extraction column and 10 stages for the vacuum distillation at P= 0.05 atm were required. To obtain the optimal ScE-Vc flowsheet section it was necessary to vary, first, the operating pressure of the ScE column from 5 to 40 atm and, monitoring the amount of triglyceride at the top of the column and secondly, the amount of CO2/methanol ratio (from 0 to 10) fed to the SCE column was adjusted, observing the purity of the triglycerides at the bottom of the column. Also, for the Vc distillation column the operating pressure was modified (from 1 to 0.02 atm) and the purity of the FFA at the top of the column was checked. It should be pointed out that PURGE1, PURGE 2 and SEP equipments can be considered as specific membranes to separate the residual CO2 streams.

 Figure 2. Optimal ScE-Vc flowsheet section obtained after intensive simulation. Stream PUR-TRIG is cooled to 70 C and sent to the second section.

Figure 3 shows the optimal RD section after intensive simulation to produce ultra-clean biodiesel and glycerol. In order to obtain the optimal RD flowsheet section, it was necessary to vary the number and location of the reactive stages monitoring the triglyceride conversion and the biodiesel purity. For the CD-GLYCE conventional column the number of stages was adjusted observing the purity of glycerol produced. It should be mentioned that 20 equilibrium stages for the RD column at P= 1 atm (reactive stages from 4 to 18) were needed to achieve a full conversion of the triglyceride mixture to biodiesel.

Figure 3. Optimal RD flowsheet section obtained after intensive simulation.

* 1. Results and discussion

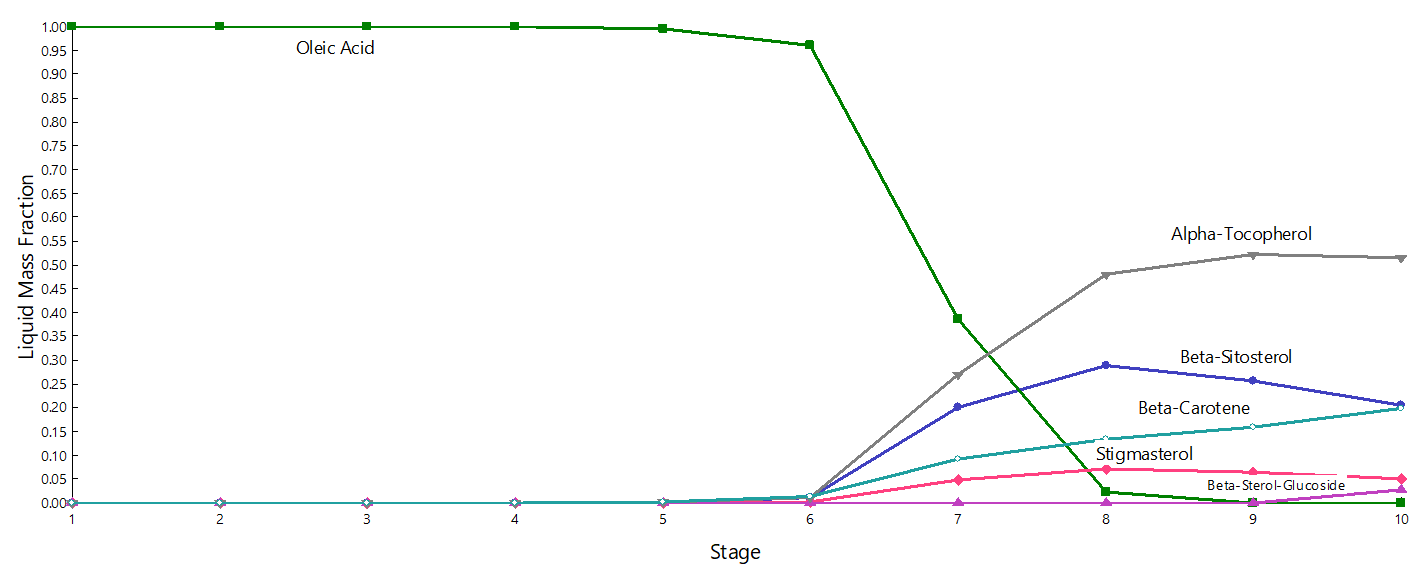
The final simulation results for each optimal flowsheet sections were obtained by using Aspen-Plus V 10.0 with the RK-Aspen Equation of State for super critical extraction and vacuum distillation and NRTL-RKS model for the reactive distillation process.

* + 1. ScE-Vc section: Production of pure triglycerides and phyto-sterols

Table 2 shows the simulation results for the ScE-VcD section to produce pure triglycerides and the separation of phytosterols from FFA. It can be noted from Table 2 that the stream PUR-TRIG only contain triolein and tripalmitin. Also, from Table 2 it can be noted that streams PURE-FFA and STER-CA contain only oleic acid at 250 C and sterols, part of carotene and the non-acylated glucoside at 368 C, respectively. Figure 4 shows the liquid composition profile for the VcD column and it can be observed that at the top of the column the oleic acid composition is 1 (pure) and at the bottom a mixture of sterols, carotene and non-acylated glucoside are obtained.

Table 2. Simulation results of the integrated-intensified ScE-VcD section. Calculations were performed using RK-Aspen Equation of State

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Material** | | | | | | | | |
| **Steam Name** | **Units** | **BOIL-STE** | **F-CO2** | **OLE-STER** | **TRIGLY** | **PUR-TRIG** | **PURE-FFA** | **STER-CA** |
| **From** |  |  |  | EXTRACT | EXTRACT | PURGE-1 | VAC-CD | VAC-CD |
| **To** |  | EXTRACT | EXTRACT | VALV-2 | VALV1 |  |  |  |
| **Stream Class** |  | CONVEN | CONVEN | CONVEN | CONVEN | CONVEN | CONVEN | CONVEN |
| **Phase** |  | Liquid Phase | Vapor Phase | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase |
| **Temperature** | C | 96.85 | 96.85 | 96.7451 | 96.85 | 180 | 250.074 | 368.218 |
| **Pressure** | atm | 30 | 30 | 30 | 30 | 1 | 0.05 | 0.05 |
| **Molar Vapor** |  |  |  |  |  |  |  |  |
| **Fraction** |  | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| **Average MW** |  | 775.878 | 42.1219 | 42.149 | 156.9 | 845.526 | 282.467 | 446.843 |
| **Mass Flows** | kg/h | 1000 | 50000 | 49751 | 1249.01 | 953.46 | 44.1212 | 1.93867 |
| **Mass Fractions** |  |  |  |  |  |  |  |  |
| **B-SITOST** |  | 0.0004 | 0 | 8.04E-06 | 1.41E-129 | 0 | 8.38E-20 | 0.206327 |
| **OLEIC-AC** |  | 0.044125 | 0 | 0.000886917 | 1.18E-115 | 0 | 1 | 2.28E-05 |
| **STIGMSTE** |  | 0.0001 | 0 | 2.01E-06 | 7.87E-132 | 0 | 1.53E-20 | 0.0515819 |
| **TRIPALMI** |  | 0.465289 | 0 | 5.63E-10 | 0.372527 | 0.488 | 0 | 0 |
| **TRIOLEIN** |  | 0.488172 | 0 | 1.78E-13 | 0.390848 | 0.512 | 0 | 0 |
| **CO2** |  | 0 | 0.88 | 0.878742 | 0.225549 | 0 | 0 | 0 |
| **B-SG** |  | 5.50E-05 | 0 | 1.11E-06 | 6.02E-10 | 0 | 3.52E-47 | 0.0283676 |
| **ACYL-SG** |  | 0.00036 | 0 | 7.24E-06 | 1.79E-69 | 0 | 0 | 0 |
| **A-TOCOPH** |  | 0.001 | 0 | 2.01E-05 | 4.26E-127 | 0 | 2.70E-20 | 0.5158190 |
| **B-CAROTE** |  | 0.0005 | 0 | 1.00E-05 | 9.85E-09 | 0 | 9.25E-12 | 0.197882 |
| **CH3OH** |  | 0 | 0.12 | 0.120323 | 0.0110759 | 0 | 0 | 0 |

Figure 4. Liquid composition profile of the vacuum distillation column

* + 1. RD section: Production of ultra-clean biodiesel and glycerol

For the RD section, the reaction kinetics for the conversion of triglycerides to biodiesel were taken from Dosin et al. (2006). Table 3 shows that the bottom stream RD-BOTT is concentrated (mass fraction) in biodiesel (methyl oleate and methyl palmitate) with little amounts of methanol and glycerol at 115 C, while at the top of the RD column pure methanol is obtained and it can be recycled to the ScE column in the first section. After cooling and decanting the RD-BOTT stream pure biodiesel is produced and the residual glycerol and methanol are separated in a conventional distillation column.

Figure 5a shows the liquid composition profile (mass fraction logarithmic plot) of the RD column. It can be noted that at the top of the column pure methanol is obtained and at the bottom of the RD column a mixture of methyl oleate, methyl palmitate, glycerol and methanol is obtained.

Table 3. Simulation results of the RD section. Calculations were performed using NRTL-RKS model.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Material** | | | | | | | | |
| **Steam Name** | **Units** | **MEOH** | **TRIGLY** | **RD-BOTT** | **RD-DIST** | **P-BIODIE** | **P-GLYCER** | **RE-OH** |
| **From** |  |  |  | RD-TRANS | RD-TRANS | DECANTER | CD-GLYCE | CD-GLYCE |
| **To** |  | RD-TRANS | RD-TRANS | COOLER |  |  |  |  |
| **Stream Class** |  | CONVEN | CONVEN | CONVEN | CONVEN | CONVEN | CONVEN | CONVEN |
| **Phase** |  | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase |
| **Temperature** | C | 65 | 70 | 115.632 | 64.2006 | 70 | 287.205 | 64.2122 |
| **Pressure** | atm | 1.3 | 1 | 1 | 1 | 1 | 1 | 1 |
| **Average MW** |  | 32.0422 | 845.526 | 163.745 | 32.0422 | 283.186 | 92.0947 | 32.0697 |
| **Mass Flows** | kg/h | 300 | 953.459 | 1140.5 | 112.955 | 958.005 | 103.747 | 78.7521 |
| **Mass Fractions** |  |  |  |  |  |  |  |  |
| **TRIOLEIN** |  | 0 | 0.512 | 0 | 1.15E-35 | 0 | 0 | 0 |
| **METHANOL** |  | 1 | 0 | 0.0689592 | 1 | 0 | 4.08E-08 | 0.998681 |
| **GRYCEROL** |  | 0 | 0 | 0.0910568 | 2.24E-32 | 0 | 1 | 0.00131886 |
| **METHY-OL** |  | 0 | 0 | 0.42998 | 3.85E-36 | 0.51189 | 0 | 0 |
| **TRIPA-01** |  | 0 | 0.488 | 6.73E-20 | 1.05E-35 | 0 | 0 | 0 |
| **METHY-PA** |  | 0 | 0 | 0.410004 | 3.21E-29 | 0.48811 | 0 | 0 |

Figure 5a. Liquid composition profile for the reactive distillation column.

* 1. Conclusions

A novel intensified-integrated ScE-VcD-RD process to produce phytosterols (β-sitosterol and stigmasterol), glycerol and ultra-clean biodiesel from crude vegetable oils has been developed. A CO2-CH3OH mixture was used as supercritical fluid for the separation of triglycerides from phytosterols, phyto-glucoside compounds and fatty acids (FFA). It was found that for 1000 Kg/h of vegetable oil fed To the ScE Column an amount of 50 times of the supercritical fluid mixture was required to fully separate the triglycerides in a 30 equlibrium stages ScE column at 30 atm. Further, the separation of phytosterols, SGs compounds and FFA by a 10 equilibrium VcD colum is performed at 0.05 atm. It should observed that part of the β-carotene is eliminated in the ACYLATED stream. In the RD column second section the triglycerides transesterification reactions to produce ultra-clean biodiesel and glycerol using a 20 equilibrium stages RD column. Such 20 equilibrium stages with 15 reactive stages were needed to fully convert the triglycerides present in the vegetable oil. It should br pointrd out that the Sc fluid mixture CO2-CH3OH can be recycled from the FLASH1 and FLASH2 in the ScE-VcD section and methanol can be recycled to the RD column in the Rd section. Future work is planned to consider the economical and energy evaluation of the integrated-intesified process and also, to incorporate a section of CO2 capture for environmental improvement.

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