Fuel Processing Technology 140 (2015) 252–261

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Study of an energy-integrated biodiesel production process using supercritical methanol and a low-cost feedstock

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ARTICLE INFO

Article history:
Received 17 June 2015
Received in revised form 14 August 2015
Accepted 23 August 2015
Available online 21 September 2015

Keywords:
Biodiesel
Supercritical methanol
Energy integration

ABSTRACT

The supercritical biodiesel production process has some disadvantages such as: high reaction temperature, large molar methanol-to-oil ratios (R) and large energy consumption. To mitigate these problems, an energy integrated process in which biodiesel is obtained in a continuous tubular reactor operating at a reaction temperature of 280 °C, R = 20, a residence time of 1 h and a pressure of 110 bar, is proposed. A low-cost lipid feedstock (chicken oil) was used as raw material for testing the process. The enthalpy content of the stream exiting the supercritical reactor was used to eliminate the unreacted methanol in an adiabatic flash drum. The operating conditions of the adiabatic flash were optimized to meet the specification of water and methanol content in the biodiesel phase and minimize the ester and acid content in the vapor phase. These conditions were: P = 0.1 bar and T = 178 °C. For these conditions the methanol content is 88–90% in the vapor phase and lower than 0.2% in the biodiesel phase. A scheme was developed for an energy integrated process maximizing the heat recovery. Composition, temperature and pressure of the streams were determined and also the amount of heat exchanged in each unit. In order to fulfill the quality restrictions the final content of FFA in the biodiesel product had to be further adjusted by adsorption over bleaching silica.

1. Introduction

Biodiesel is a renewable fuel [1] generally comprising a mixture of fatty acid methyl esters that is produced by reacting glycerides from biomass, such as animal fats or vegetable oils, with an alcohol, usually methanol [2], in the presence or not of a catalyst.

Transesterification with homogeneous strong alkali catalysts is the most widely used industrial technique for producing biodiesel because of some advantages such as a shorter reaction time, higher conversion rate, and a smaller amount of catalyst, as compared to other catalytic processes [3,4]. On the other side, the so-called supercritical method does not use any catalyst [5]. The supercritical method has from the beginning been associated to short reaction times (a few minutes). In order to have a high reaction rate, high methanol-to-oil ratios are employed, that lead to high pressures, elevated energy costs (high reaction temperature) and the need to recycle the large excess of unreacted methanol [6]. These problems severely restrict the supercritical method for the industrial production of biodiesel and there are no commercial biodiesel production facilities currently using the supercritical method. This is partly due to the high energy needed to run the reactor at high temperature and pressure and sustain the supercritical state. In this sense the means to achieve the recycle of high-temperature and high-pressure methanol is a key factor for solving the problem of high energy consumption and high production cost [7]. However many advantages of the supercritical process should be acknowledged, the main one being the ability to process low quality feedstocks. This is especially important because the price of biodiesel depends 80–90% on the value of the lipidic raw feedstock used.

Of all possible low-cost feedstocks, chicken oil obtained from the steam autoclave treatment of chicken viscera is a feedstock worth to be considered for biodiesel production. It has a major composition of oleic acid methyl ester which is an advantage in comparison with some vegetable oils. Important biodiesel properties such as the oxidation stability, cloud point and cetane number are improved using this raw material.

One important aspect of the biodiesel process is that the net yield of fatty acid methyl esters must be high enough for making the process competitive [8]. As alkaline catalysts are very sensitive to water and free fatty acids (FFA) the percentage of water and FFA in the feedstocks of alkali-catalyzed reactors must be lower than 0.06% (w/w) and 0.5% (w/w), respectively. Otherwise the ester yield is decreased by side reactions during the catalytic transesterification reaction. In the case of the supercritical method the FFA and water contents have no negative effect on the reaction rate or the ester yield. Moreover water and FFA can give impetus to the reaction under certain conditions. For instance chicken oil and frying oil with very high FFA and water contents have been reported to be easily transformed into biodiesel with supercritical methanol [9].

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http://dx.doi.org/10.1016/j.fuproc.2015.08.026
0378-3820/

The objectives of this work are many: (i) Study the properties of biodiesel produced by supercritical transesterification of a high acidity, low cost raw material (chicken oil). (ii) Elucidate the network of chemical reactions taking place in the supercritical reactor with the aid of chromatographic compositional data and a thermodynamic analysis. (iii) Propose a process layout of low energy consumption that enables the production of biodiesel technically compliant with the quality standards. The process synthesis effort will be aided by computer simulation of the reactor, the separation units and the heat exchangers. A mathematical optimization will be performed for minimizing the energy consumption of the process.

Particularly the conditions are studied in which the enthalpy of the reactor product stream is high enough for eliminating residual methanol and water in adiabatic flash drums; at least in an amount sufficient for reaching the limit content values of quality norms. Adiabatic flash drums should enable big energy savings and reduce the heat load of the process. After verifying the validity of the use of adiabatic flash stages a process layout will be proposed using units for reaction, separation and heat recovery. After this, additional steps could be needed for adjusting the final content of the impurities to the desired level. This will be preferentially done by using adsorption units as proposed elsewhere [9].

In comparison to other published reports the current work is a proposal of an energy-integrated process using milder reaction conditions, i.e. lower methanol-to-oil ratio, temperature and pressure. This translates into savings in pumping, methanol recycling and heating/cooling. Another difference is that adsorption instead of washing is chosen as unit operation for adjusting impurity levels in the produced biodiesel. This should lead to a reduction in the volume of generated wastewater and the cost of wastewater treatment and disposal.

2. Materials and methods

2.1. Materials

Chicken oil (24.0% free fatty acids (FFA); 75.8% triglycerides (TG), 0.12% water, 100 iodine value, 33 cSt viscosity) was supplied by Granjas Carnave S.A. (Esperanza, Argentina). This product was obtained by steam autoclave treatment of chicken viscerae. Methanol (>99.9%) was supplied by Dorwil.

2.2. Transesterification reaction

Oil and methanol were placed in a stainless steel autoclave reactor of 50 mL having a thermocouple and a pressure gauge. The amounts of oil and methanol were regulated in order to yield a value of the molar methanol-to-oil ratio (R) of 20. After charging the reactor, the top flange was put and tightened, nitrogen was introduced for purging and all valves were closed. Then the reactor was heated from room temperature to the target temperature (280 °C) at a heating rate of 30 °C min^{-1}. The mixture was allowed to react at the autogenous pressure of the closed system (110 bar) for 1 h. Then the reactor was rapidly transferred to an ice bath to quench the reaction. Once the reactor was cold the top flange was removed and the liquid content was transferred to an Erlenmeyer. The oil was weighed to determine the liquid yield of the reaction. The amount of light gases formed was determined from a mass balance. Reaction tests were performed in triplicates in order to decrease the experimental error. A more detailed description of the used equipment and procedure can be found elsewhere [8].

2.3. Refining steps and tests for methanol balance

The liquid product mixture was first transferred to an atmospheric distillation apparatus. The column was entirely made of Pyrex glass and comprised a spherical reboiler, a multilobe column and a Liebig condenser. These parts and the heating and cooling units were built according to the ASTM D86 standard. A reboiler temperature of 100 °C, a condenser temperature of 20 °C and a distillation time of 1 h were used to separate the unreacted methanol and other volatile compounds from the rest of the biodiesel phase. The recovered methanol solution and the distilled biodiesel were then weighed separately. The biodiesel phase was left unstirred for 6 h to allow the glycerol phase, if not completely decomposed, to decant to the bottom of the flask as a separate layer. The upper biodiesel layer was then sampled for analysis.

Unreacted methanol separated by the above distillation procedure was analyzed by gas chromatography in a Varian 3800 equipped with a mass spectrometry Saturn 2000 detector.

2.4. Analysis of biodiesel

Samples of biodiesel were analyzed according to different standard techniques as indicated by the quality norms [10,11]. Maximum allowed values as well as the results, are indicated in Table 1.

2.5. Process simulation

The proposed energy integrated biodiesel production process with the involved units is depicted in Fig. 1.

The whole process was simulated using the software UNISIM DESIGN 349. For calculation purposes almost all process units were considered to operate in a continuous fashion. Serial tank bleachers, operated in discontinuous mode, were simulated separately using Matlab for Windows R2013b.

The conditions and composition of the stream entering the expansion valve (VLV-1) were determined taking experimental results into account. The inlet temperature was not fixed and was a variable of the optimization procedure. The simulation methodology involved varying the pressure drop in the inlet valve and obtaining different pressure, temperature and composition values at the exit of the drum.

The flash drum was modeled on the basis of classical liquid–vapor equilibrium. Physical property data of the involved compounds (methanol, glycerol, water, etc.) were taken from the UNISIM property libraries. With respect to the methyl esters, methyl oleate was taken as a model compound for representing biodiesel. Hydrogen and carbon dioxide were the only gaseous compound considered. The thermodynamic properties were estimated using group contribution properties [12].

Due to the presence of highly polar compounds such as methanol and glycerol, and the widely different size of some molecules in the mixture, the solutions were non-ideal. This non-ideality was accounted for by means of activity coefficients. The activity of the compounds in the liquid phase was described using the NRTL (non-random two liquid) or the UNIQUAC (universal quasi-chemical) models. The vapor–liquid

Table 1
Physical and chemical properties of the raw biodiesel obtained by transesterification of chicken oil. Reaction conditions: 280 °C, 110 bar, methanol-to-oil molar ratio, 20.

Property	Norm method	Norm values	Experimental values
Methyl ester content, % (w/w)	EN 14103	>96.5	97.0
Density at 15 °C, kg/m^3	EN ISO 3675	860–900	876
Viscosity at 40 °C, mm^2/s	D445	1.9–6	5.7
Flash point, °C	D93	>130	163
Sulfated ash, % (w/w)	D874	<0.02	0.015
Conradson carbon, % (w/w)	D4530	<0.05	0.02
Water content, mg/kg	D2709	<500	**800**
Free fatty acid content, %	D664	<0.40	**2.7**
Iodine value	EN 14111	<120	100
Methanol content, % (w/w)	EN 14110	<0.2	0.15
Free glycerol, % (w/w)	D6584	<0.02	0.019
Total glycerol, % (w/w)	D6584	<0.24	0.17