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Biodiesel production from tomato seed by transesterification with alkaline and 'green' catalysts: simulation and discussion

Marcello Casa *, Chiara Prizio , Michele Miccio

Dipartimento di Ingegneria Industriale, Università di Salerno, Via Giovanni Paolo II, 132 - 84084 Fisciano (SA)
mcasa@unisa.it

The aim of this work is to model a more environmental-friendly production of biodiesel from tomato seed oil to assess the feasibility of using an alternative catalyst. The AspenPlus® software is used to this end. Different cases are evaluated and compared, by changing the catalyst and by considering the additional production of high purity glycerol and potassium phosphate. Tomato seed oil obtained from tomato pomace coming from local industries, methanol and catalyst are considered as raw materials. Based on literature data, a methyl-esters yield formulation is developed and the catalytic transesterification reaction implemented in a simulated reactor, while methanol is recovered by distillation and recycled to the reactor. The necessary distillation towers are designed. All the mass and energy balances were set up for the whole process. The energy return of investment (EROI) was determined by considering the energy for harvesting and that for producing biodiesel. Results show that tomato seed oil can be a feasible alternative for biodiesel production.

1. Introduction

The use of vegetable oil for biodiesel production can play an important role in developing a new ecofriendly system fostering the transition to renewable energy (Mishra and Goswami, 2018). Biodiesel is obtained as the result of a chemical reaction, namely alcoholysis or transesterification, between the triglycerides, contained in the starting oil, and alcohol. The transesterification of the triglycerides is usually carried out with a catalyst to reach a reasonable reaction rate (Mumtaz et al., 2017). From the catalytic transesterification process crude glycerol is obtained as a reaction byproduct containing 70-80% of glycerin, in addition to resulting amounts of water, catalyst, FFA and salts. A purification process of glycerin, up to 98%, enables its use in the most diverse areas, in particular in the pharmaceutical and food processing field (Monteiro et al., 2018).

The reaction is performed at a temperature close to the boiling point of the alcohol and pressures slightly higher than atmospheric, ensuring that it takes place in a liquid phase. The alcohols typically used for the reaction are butanol, ethanol, and methanol. Methanol is often preferred due to the lowest cost, which is a significant feature because reaction requires a high amount of alcohol to ensure high yield, moreover, it avoids the formation of undesired emulsions and thus facilitates the separation of the reaction products (Meher et al., 2006).

Catalysts may be acid, basic or enzymatic. The catalyst amount can be adjusted to reach the desired conversion of the product, but generally the optimum catalyst corresponds to concentration ranges between 0.5 and 1%wt. Base-catalyzed transesterification allows higher rates and, consequently, better performance. It is characterized by a less corrosive nature of the used reagents and lower costs related to purchasing and transport, as well as subsequent disposal stage. The most studied and used alkaline catalysts are sodium and potassium hydroxides (NaOH and KOH) (Mumtaz et al., 2017). On the other hand, a heterogeneous catalyst as the alkaline one could lead to higher costs for the separation of the reaction media as they are partially miscible in reaction products. Homogeneous catalysts have been recently studied and tested as alternatives. These studies show that "eggshell" or "fish and chicken bones" can be used as starting materials for the production of catalyst for transesterification, leading to comparable biodiesel yield, easy separation steps, and a more sustainable process, by avoiding the burden of wasting these materials (Tan et al., 2019).

Regarding the organic feedstock, edible oils, in particular soybean, palm and rapeseed oil are the mainly used vegetable oil for this process, guaranteeing high biodiesel yields with the use of alkaline catalysts, thanks to their low Free Fatty Acid (FFA) content. However, the disadvantage of these raw materials is the high cost and the competition that is created between oils intended for human consumption and those subtracted from it to produce biodiesel (Gupta et al., 2016).

For these reasons many efforts have been made by researchers and industries to find alternative oils, coming from waste streams, but ensuring reasonable yields with mild reaction conditions (Bhuiya et al., 2016). A valid example is provided by the WCO (waste cooking oil) or spent cooking oil, which is not intended for human consumption and is advantageous for its low cost (compared to virgin vegetable oil). Moreover, the use of this kind of feedstock prevents its landfilling or, even worse, its incorrect disposal, by avoiding unwanted noxious emissions (Bhuiya et al., 2016). Recently tomato seed oil (TSO), an underused and wasted vegetable oil, was proposed as an alternative feedstock to produce biodiesel, due to its characteristics and easiness of extraction from tomato peels. Moreover, it was demonstrated that the physicochemical properties of tomato seed oil are within the standard for rapeseed oil currently used for biodiesel production in Europe (Giuffrè et al., 2016) and it was showed that the esterification of tomato seed oil could lead to the production of biodiesel that meets European legislation (Giuffrè et al., 2017). To the best of the authors' knowledge, no studies or research were carried out to investigate the scalability and the technical and economic feasibility of a process plant producing biodiesel and glycerol from tomato seed oil as feedstock. Therefore, this work reports about the conceptual development and optimization of a plant producing biodiesel and glycerin with pharmaceutical grade. Such a projected plant can be viewed as a section dedicated to the production of biodiesel and glycerine within a biorefinery layout designed for the whole valorization of tomato processing residues and summarized in a previous paper (Casa et al., 2020a). The use of two different catalysts is proposed: a conventional heterogeneous catalyst and a "green" alternative. Therefore, two flowsheets are developed; the technical feasibility of the processes is discussed; the EROI index assessing the energetic feasibility is evaluated. The Aspen Plus® software was smartly employed to carry out simulation and optimization of processes.

2. Materials and methods

2.1 Feedstock characteristics

As a basis for calculations, the amount of tomato seed oil (TSO) to be processed is 390 ton/y, namely 69.7 kg/h. This is the amount of TSO in tomato by-products generated by 5 medium-to-large factories during a two-month working season located in Campania in a small area with a diameter of 10 km. The composition of the oil was considered as the one reported by Giuffrè et al. (2016), with trilinolein as the main component, a moisture content as low as 0.5%wt and a free fatty acid content lower than 2%.

2.2 Transesterification reaction: parameters and yield

Two different scenarios for the transesterification reaction were considered: the first in which the reaction is catalysed by potassium hydroxide (KOH) in a homogeneous way and the second in which the reaction is catalysed in a heterogeneous way by calcium oxide (CaO), this latter being obtained by wasted eggshells. The conditions for the first scenario were gathered by the experimental research of Giuffrè et al. (2017). In particular, a reactor temperature of 55°C, a methanol/oil ratio of 6 and KOH content of 0.1% on weight basis were considered; moreover, with a residence time of 1 h, a reaction yield of 96.2% was assumed (Giuffrè et al., 2017). Regarding the second scenario the key parameters were inferred by two experimental works on transesterification of vegetable oils (Fayyazi et al., 2018; Kouzu et al., 2009). In particular, a reactor temperature of 60°C, a methanol/oil ratio of 6.03 and a CaO content of 0.2% on weight basis were considered; moreover, with a residence time of 2 h, a reaction yield of 96.5% was assumed (Fayyazi et al., 2018; Kouzu et al., 2009).

2.3 Process simulation

Process flowsheeting was carried out to assess the technical feasibility of the biodiesel production, with a quality meeting European standard, and glycerin, with pharmaceutical grade, from tomato seed oil and, hence, allowing the comparison of the scenarios. The simulation was performed with Aspen Plus®. The method selected to describe the liquid phase was NRTL (Non-Random Two Liquid Model), because it allows a good simulation of the interaction between components, even if they have high polarity like methanol and glycerin. For the tomato seed oil, trilinolein, included in the *Biodiesel* database of Aspen Plus® was used as a representative component. With this background the two scenarios for biodiesel production were implemented in Aspen Plus®. Both schemes can be divided into 5 main sections (see Figure 1):

- Transesterification reaction: in this section the feedstocks are sent to the reactor, the reaction conditions are set, and the tomato seed oil is converted to biodiesel and glycerine.
- Washing: water is used to enable phase separation, to obtain a biodiesel-rich and a glycerine-rich phase
- Biodiesel purification: in this section the biodiesel is purified from minor substances through a distillation under vacuum and a sedimentation step

- Catalyst recovery: the homogeneous catalyst (KOH) is neutralized with an acid and recovered as a salt, while the heterogeneous catalyst (CaO) is separated by centrifugation and recycled to the reactor
- Glycerin purification: glycerine purity is brought up to 98% via a series of distillation steps removing residual methanol and water. The methanol is recovered and sent back to the reaction section.

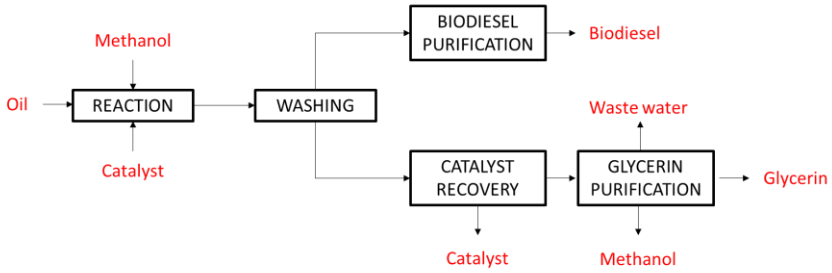

Figure 1 Simplified block diagram for biodiesel production from tomato seed oil

For the sake of clarity and readability, the two main flowsheets developed in Aspen Plus® are not reported in the text but highlights of the main sections are shown and discussed in the following.

2.4 EROI evaluation

A required evaluation for a plant proposed for producing fuel is the EROI index, namely the energy return of the investment. It allows assessing if the energy spent to produce that fuel (including the energy needed to harvest the raw material fed to the process) is lower than the energy released by the combustion of the same. In this work the EROI is evaluated with the following equation:

$$EROI = \frac{LCV_{biodiesel} \times F_{biodiesel}}{E_{harvesting} + E_{tansport} + E_{transeterification}} \qquad (1)$$

where $LCV_{biodiesel}$ is the lower calorific value of biodiesel. $F_{biodiesel}$ is its mass flow rate, $E_{harvesting}$ is the energy needed for harvesting tomato (allocated for TSO mass flow rate) (Campiotti, 2016), $E_{tansport}$ is the energy needed to transport tomato by-products to the production plant and $E_{transesterification}$ is the energy for operating the production plant. The EROI index must be greater than 5 for non-renewable energy sources in order to rate the fuel production plant technically feasible (Rana et al., 2020).

3. Results and discussion

The first section implemented in the software is the reaction section, which is reported in Figure 2.

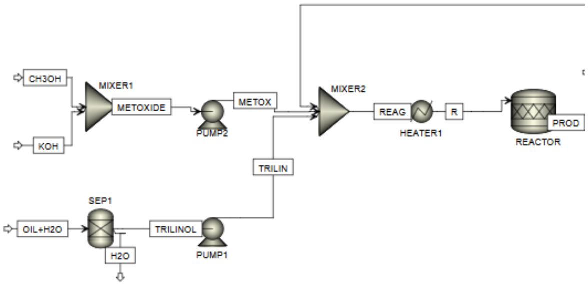

Figure 2 Highlight of the reaction section for the first scenario

Here, the unwanted water, although as small as 0.5 %wt., is removed by the TSO stream by sedimentation and the purified stream is pumped to the reactor. Methanol and catalyst are mixed to allow the formation of the active species. Then, the reaction media are mixed with the oil and brought to the optimal reaction conditions. The temperature is around 60°C for both scenarios, to keep the reaction mixture near to the methanol boiling condition. The pressure is set as 4 bar for the heterogeneous catalyst and 1 bar for the homogeneous catalyst to optimize the process yield as reported in the literature (Fayyazi et al., 2018; Giuffrè et al., 2017; Kouzu et al., 2009). The transesterification reactor was simulated by the means of an ideal block, i.e., *RStoic*, in Apsen Plus®, which requires as input the operating conditions and the stoichiometric reaction with the relative yield. Here the transesterification of trilinolein into its methyl ester and glycerin was considered:

$$C_{57}H_{98}O_6 + 3CH_3OH \rightarrow 3C_{19}H_{34}O_2 + C_3H_8O_3 \tag{2}$$

The reaction conversion was set 96.2% for the reaction with KOH as the catalyst and 96.2% for the reaction with CaO. The reactor outlet (PROD) contains the products (biodiesel and glycerin) and the unreacted reagents. Since the two products are partially miscible, their separation is induced through a water washing unit, since glycerin is hydrophilic. At the industrial scale, the separation of the methyl esters and glycerin is carried out with centrifugation because natural occurring sedimentation of the phases would be too slow. Figure 3 shows the washing section.

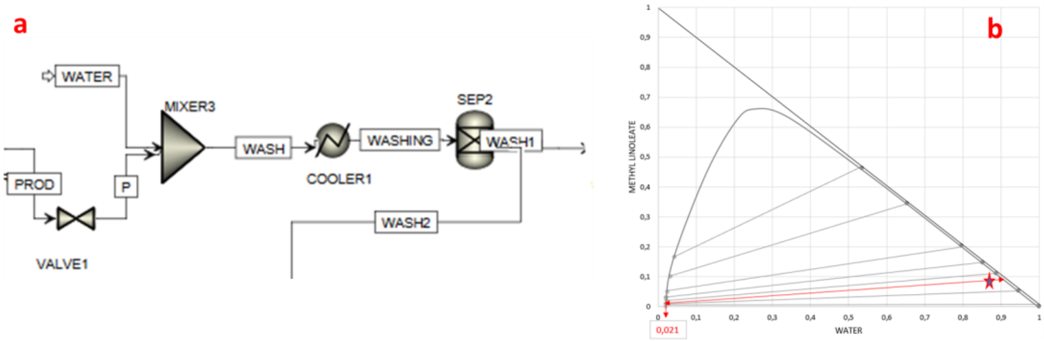

Figure 3 a) Highlight of the washing section, b) LLE equilibrium diagram: the red star indicates the stream entering the SEP2

The optimal value of the water feed rate (WATER) was evaluated with the *Sensitivity* tool of the software that allows performing a 'what if' analysis by varying a parameter. In the specific case, the water flow varied in a range of defined values, in order to choose the minimum flow rate that would allow the highest recovery in biodiesel. The optimum water flow rate was found to be 36.9 kg/h for both scenarios. The *split fraction* implemented in SEP2 block was based on the *water-methanol-methyl linoleate* liquid-liquid equilibrium (LLE) data, as reported in the literature, used for the construction of the triangular diagram reported in Figure 3b (Lee et al., 2010). In this way, it was possible to draw the miscibility gap and the tie-lines, to evaluate the fraction of water and methanol in biodiesel (WASH1), and in glycerin-rich phase (WASH2) by difference. For both scenarios, the water molar fraction in biodiesel is 0.021 while that one for methanol is 0.0369. WASH1 and WASH2 are sent to the biodiesel purification and glycerin purification sections, respectively.

The methyl ester-rich stream, identified in the flowsheet as WASH1, contains biodiesel (methyl linoleate in the simulation), and small amounts of methanol and water. This stream is sent to a distillation tower for the separation of biodiesel, i.e., RADFRAC1. Then the distilled biodiesel is furtherly purified from remaining free fatty acid impurities by means of centrifugation (SEP3), as reported in Figure 4.

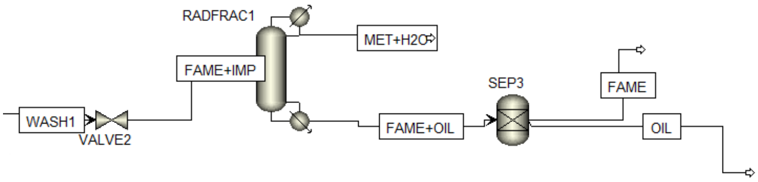

Figure 4 Highlight of biodiesel purification section

The operating conditions of the distillation tower are reported in the following table:

Table 1: Operating condition of the distillation tower for biodiesel purification

Temperature	Pressure	Stage Number	Reflux ratio
50 °C	0.01 bar	8	8.5

Temperature is set the same as the WASH1 temperature, while the pressure is kept below the atmospheric one and selected to have the temperature of the bottom stream consistently lower than the degradation temperature of biodiesel. The stage number (N) and reflux ratio (R) were optimized by means of a series of sensitivity analyses in order to have a methyl ester recovery in the bottom stream higher than 0.9975 and the minimization of the heat at the reboiler (9.98 kW). The MET+H2O stream is considered wastewater and sent to disposal as the OIL stream (containing impurities), while the FAME stream provides a recovered product at 100% of purity with a mass flow of 67.7 kg/h for both scenarios.

The glycerine in the WASH2 stream, coming from reaction section and the washing step, has very low purity, depending on the conversion method and the type of catalyst and alcohol used. Therefore, a purification step to ensure pharmaceutical grade (higher than 98%) is mandatory. This step contains two main blocks: the first for the removal and recovery of the catalyst and a train of distillation tower for glycerine purification (Figure 5).

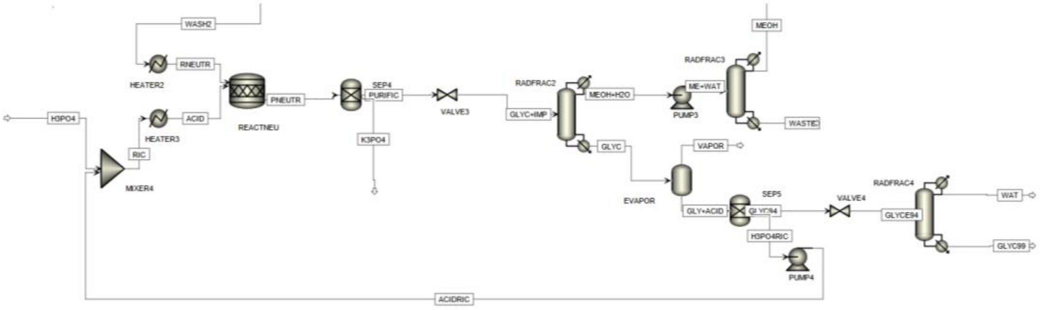

Figure 5 Highlight of glycerine purification step for first scenario

In the first scenario the KOH catalyst is neutralized by the means of the addition of phosphoric acid that reacts with the catalyst leading the formation of the phosphate salt:

$$KOH\ + H_3PO_4 \rightarrow K_3PO_4 + 3H_2O \tag{3}$$

The reaction is carried out in the REACTNU block at 60°C and 1 bar, then the salt is removed by centrifugation in SEP4. The phosphate salt is recovered with a mass flow rate of 0.3 kg/h as an important by-product due to its utilization as fertilizer. The PURIFIC stream, containing glycerine, methanol, water and unreacted acid is sent to the series of distillation columns that work at the following operating conditions, optimized with the same method reported for RADFRAC1:

Table 2 Operating condition for the distillation towers in the glycerine purification section for first scenario

	Temperature	Pressure	Stage Number	Reflux ratio
RADFRAC2	60 °C	0.05 bar	7	2
RADFRAC3	23 °C	1 bar	17	8
RADFRAC4	120 °C	0.02 bar	7	1

At downstream, methanol (99% pure) is recycled to the reactor while wastewater is sent to disposal, the acid is recycled to the neutralization reactor while 6.8 kg/h of glycerine are collected as a valuable product. In the second scenario, the CaO catalyst is removed by WASH2 stream by the means of centrifugation. Therefore, the next purification results in only two distillation towers, due to the absence of unreacted acid.

Table 3 Operating condition for the distillation towers in the glycerine purification section for the second scenario

	Temperature	Pressure	Stage Number	Reflux ratio
RADFRAC2	60 °C	0.05 bar	7	2
RADFRAC3	23 °C	1 bar	17	8

As in the first scenario, methanol is recycled to the reactor and wastewater is sent to disposal, the recovered CaO is recycled partially to the reactor while 7 kg/h of glycerine are collected as a valuable product.

After the simulation of the two scenarios that assess the technical feasibility of biodiesel production from TSO, the EROI was evaluated by using Eq.1. The energy consumption for the harvesting was considered 187 Kcal/kg, as partly allocated from tomato harvesting process, the contribution from transportation was considered negligible due to the short, while the $E_{transesterification}$ was considered as the energy needed for operating the plant (from reaction to purification step). Eventually, the EROI for the conventional scenario with KOH as catalyst was 5.83 while it was 5.5 when the alternative catalyst, CaO from eggshells, is used.

4. Conclusions

This work demonstrates the technical feasibility for industrial production of biodiesel from tomato seeds oil (extract from tomato pomace coming from an area territorially limited) using methanol in two cases differing in the approach underlying the selection of the catalyst, a traditional one (potassium hydroxide, KOH) and another "green" (calcium oxide, CaO from eggshells). The AspenPlus® software proved to be a perfect tool for simulation of the catalytic transesterification and ancillary unit operations, ensuring biodiesel productivity of 380 ton/y and glycerine production of around 40 ton/y in both scenarios. Great attention has been paid to the issue of recovery and recycle, according to a design approach complying with process integration and waste minimization. Therefore, the unreacted methanol in excess is recovered and recycled to the reactor with purity above 99% by a distillation column, ensuring its reduced consumption. Moreover, the calculated EROI values for both scenarios are higher than 5. In conclusion, these promising results show that tomato seed oil can be a viable alternative feedstock for biodiesel production.

This work could be a basis for the development and design of a multi-product biorefinery, based on tomato by-products from the canning industries located in a small territorial area. To this end, a similar paper (Casa et al., 2020b) reports about the pectin production from tomato peels in the same biorefinery framework.

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