

# Energy requirement estimates for two step ethanolysis of waste vegetable oils for biodiesel production

Nikolas Ligeris <sup>1, a</sup> and Kalala Jalama <sup>1, b</sup>

<sup>1</sup>Department of Chemical Engineering, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, Johannesburg, South Africa

<sup>a</sup>archoid2@gmail.com, <sup>b</sup>kjalama@uj.ac.za

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**Abstract.** ChemCad 6.4 simulation package was used to model a two-step biodiesel production process from waste vegetable oils (WVO) and ethanol using homogeneous acid and alkali catalysts respectively. The developed process flowsheet consisted of pre-esterification and transesterification of WVO, ethanol and glycerol recovery, and biodiesel refining. The energy required for each processing unit as well as the energy required for the whole process have been estimated. Ethanol recovery accounted for the highest portion of the energy required for the entire process estimated as 2.75 MJ per kg of biodiesel produced.

## Introduction

The interest in processes that produce biofuel grows on a daily basis around the globe as there is an urgent need to address energy challenges. Biodiesel, in particular, has received more attention as it is a bio-degradable and non-toxic fuel [1] and also because the price of fossil-derived diesel keeps on increasing. It is a mixture of methyl or ethyl esters that can be produced by the transesterification reaction of renewable feedstock such as organic oils and fats with methanol or ethanol respectively in the presence of an acid or alkali catalyst. Glycerol is also formed as a by-product of the transesterification reaction. Free fatty acids (FFA) can also be directly converted to alkyl esters (biodiesel) and water as byproduct in presence of an alcohol in the same catalytic environment as above [2]. The interest in using WVO as feedstock for biodiesel production is twofold: i) they constitute a cheap feedstock that does not compete with food production and ii) their disposal into waste drainage posing environmental problems is eliminated or reduced. The quantity of produced waste cooking oil amounts to ca. 379 million litres per day in USA [3] and 1.9 – 2.6 million gallons per day in Europe [4]. The amount of waste cooking oil available in South Africa on a monthly basis is in excess of 30 million litres [5]. Due to thermal oxidation of the triglycerides and the food's inherent water during frying, WVO often contain significant amount of FFA and water. For this reason, when WVO are used as feedstock for biodiesel production, an alkali homogeneous catalyst must not be used to avoid alkali soap formation that not only consumes the alkali catalyst but also creates emulsions which lead to difficulties in downstream recovery and purification of biodiesel [6]. For this reason, the conversion of WVO into biodiesel is usually carried in two steps consisting of a direct FFA esterification into biodiesel in presence of an acid catalyst (step 1) followed by an alkali conversion of the oil in the second step. Single-step processes for WVO conversion into biodiesel using acid catalysts have also been reported [7-9].

This work aims at using ChemCad 6.4 simulation package to model a process that uses two-step conversion of WVO into biodiesel. The first step will use an homogeneous acid catalyst for direct esterification of FFA contained in the WVO feedstock and the second step an alkali catalyst for the transesterification of triglycerides. Energy requirement for the process will be evaluated.

## Methodology

A process feed of 1050 kg/h of WVO was used for the process simulation and was modeled by a mixture of triolein (94 wt.%) and oleic acid (6 wt.%). Biodiesel was modeled by ethyl oleate and was referred to as fatty acid ethyl esters (FAEE). As this component was not available in the ChemCad component library, it was created using the Universal Functional Activity Coefficient (UNIFAC) group contribution method. The boiling point for FAEE was entered as 210°C [10], molecular weight as 310.53g/mol and SG at 60°F as 0.8773 [11]. All other components were available in ChemCad components database. The complete list of components used in the simulation is as follows: ethanol, glycerol, sulfuric acid, sodium hydroxide, water, calcium oxide, calcium sulphate, tri-sodium phosphate, triolein, oleic acid and ethyl oleate. The non-random two liquid (NRTL) model was selected as the global property model for the simulation. Where applicable, local thermodynamics were set as modified UNIFAC with a vapour/liquid/liquid/solid phase option. All binary interaction parameters (BIP's) that were not available in the simulation databanks were regressed using the UNIFAC vapour–liquid equilibrium and UNIFAC liquid–liquid equilibrium models where appropriate.

The simulated process flowsheet for the acid-catalyzed FFA esterification stage is presented in fig. 1 (step 1) and includes acid-esterification reactor (R-1), acid neutralization reactor (R-2) with gravity separator (S-1), distillation column (C-1), extraction column (W-1), heat exchanger (E-1) and pumps (P-1 to P-4).

The process flowsheet for the alkali-catalyzed transesterification stage is given in fig. 2 (step 2) and includes alkali-transesterification reactor (R-3), distillation columns (C-2 to C-4), extraction column (W-2), alkali neutralization reactor (R-4), gravity separators (S-2 and S-3), heat exchangers (E-2 and E-3) and pumps (P-5 to P-7). Reactors R-1 and R-3 were modelled as isothermal continuously stirred tanks at equilibrium conditions assuming 95% conversion of WVO to FAEE. Ethanol and H<sub>2</sub>SO<sub>4</sub> were mixed together and pumped to another mixing tank where they were mixed with the WVO. The Ethanol to WVO ratio was 6:1:1 and the amount of H<sub>2</sub>SO<sub>4</sub> used was 2.1% of the WVO. This mixture passed through a pre-heater (E-1) before being fed to the acid-esterification reactor (R-1). Downstream purification consisted of acid catalyst removal by CaO (R-2) and gravity separation (S-1), triolein feed purification by wash column (W-1) and Ethanol recovery by distillation (C-1). This triolein was mixed in a similar manner to the feed preparation steps above using a ethanol to WVO ratio of 6:1 with 1.25% NaOH. This was fed to transesterification reactor R-3. Further purification consisted of ethanol recovery by distillation (C-2), glycerol separation by washing column (W-2) and distillation(C-4), alkali catalyst removal by H<sub>3</sub>PO<sub>4</sub> (R-4) and separation (S-3) and FAEE refining (C-3). Reflux ratios were calculated using a shortcut-modelled distillation column to determine the minimum reflux ratio ( $R_{min}$ ), number of stages, feed stage location and reboiler duty. Thereafter these parameters were fed into a rigorous SCDS column model in ChemCad. For less than 50 ideal stages the reflux ration was taken as  $1.5 \times R_{min}$  and  $1.2 \times R_{min}$  for much larger columns. In the simulations, a top and bottom tray efficiency of 60 and 70% respectively were assumed with a linear efficiency profile. Because FAEE and glycerol are susceptible to thermal decomposition above 250 and 150°C respectively [12], vacuum operation for the FAEE and glycerine purification was necessary to keep the temperature at suitably low levels. ASTM standard purity for the produced biodiesel i.e. 99.65wt.% FAEE [12] was targeted in this study. Liquid–liquid extraction was used to separate FAEE from glycerol, ethanol and catalyst.

## Results and discussion

Material and enthalpy balance data for the simulated process are presented in fig. 1 and 2. About 85% of ethanol from the esterification reactor (stream 11) was recovered by distillation in column C-1 and recycled. A second step for ethanol recovery was achieved by distillation in column C-2 (fig. 2) where almost 100% of ethanol was recovered in stream 36 with a purity of ca. 98 wt.%. This purity was limited because of the water-ethanol azeotrope. No azeotropic distillation was considered in this study. The overall material balance data (fig. 1) show that ca. 0.3% of ethanol fed

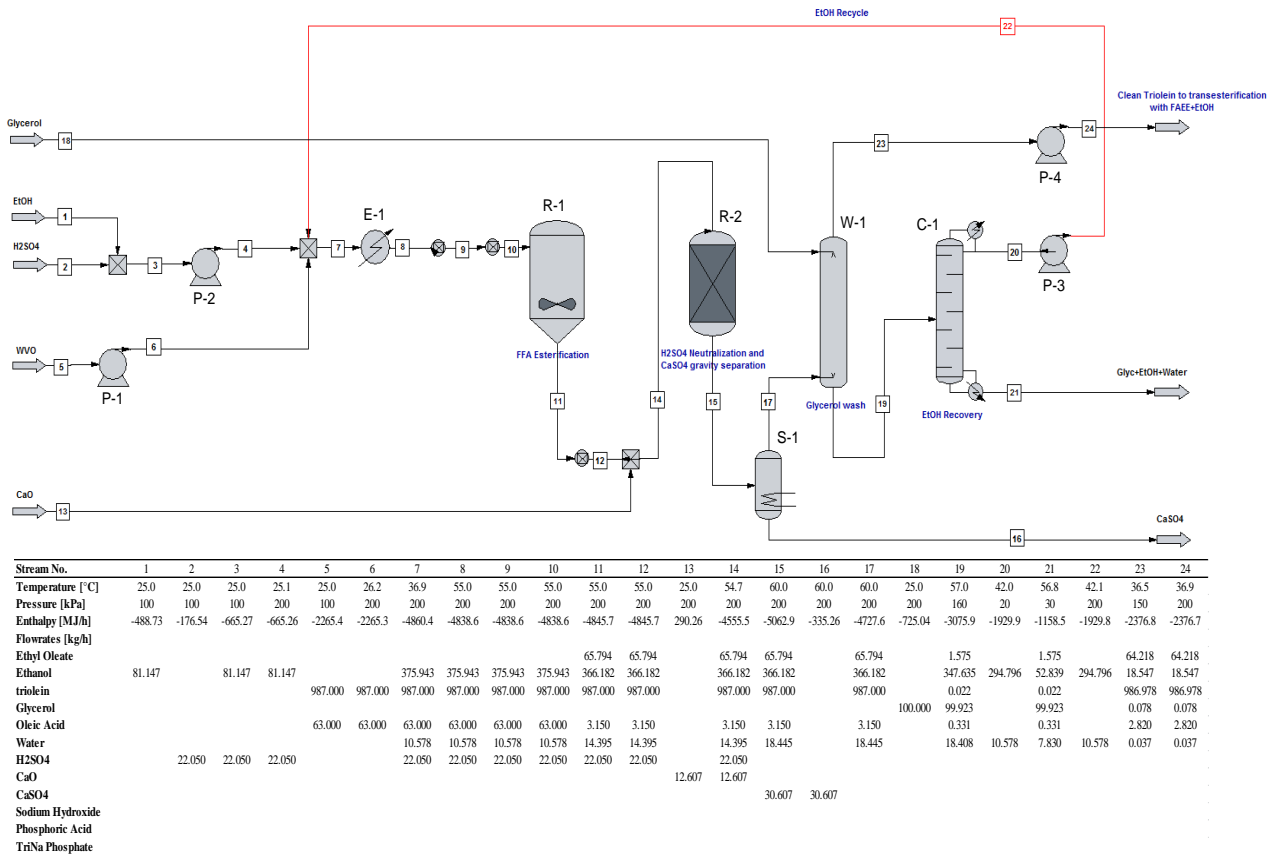


Fig. 1 Simulated flowsheet for WVO pre-esterification (step 1) with materials and enthalpy balance

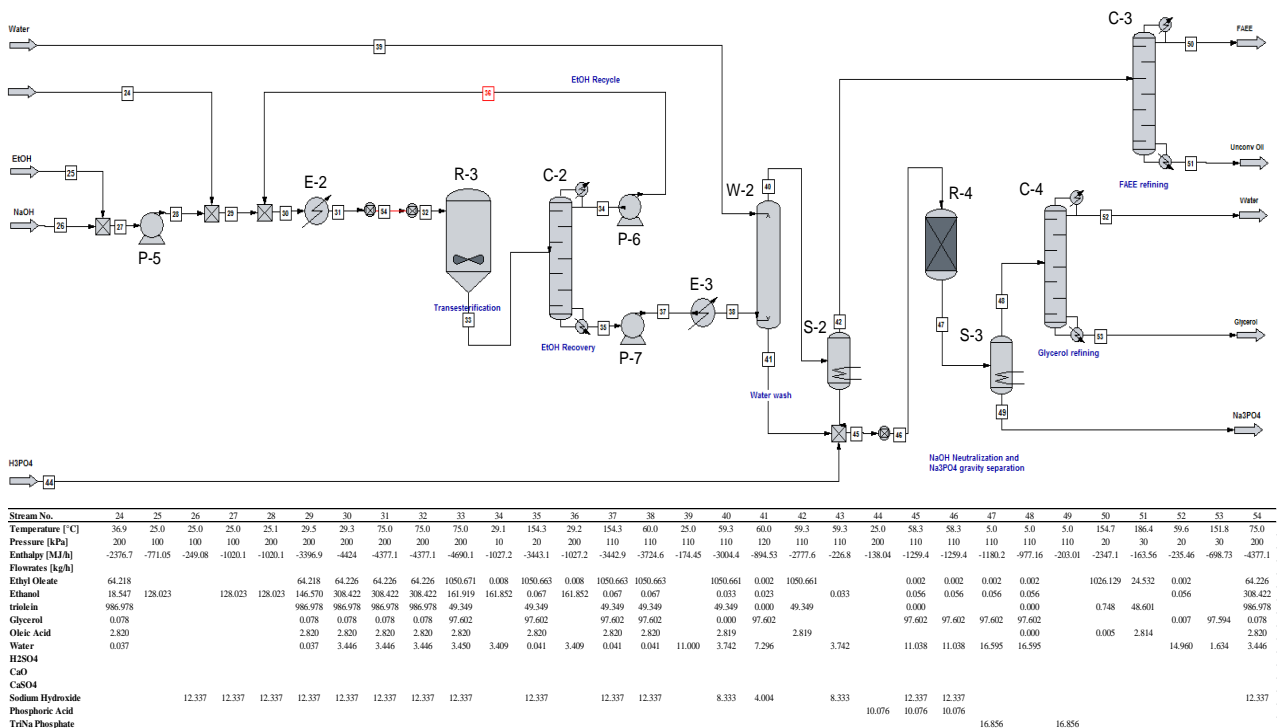


Fig. 2 Simulated flowsheet for alkali catalyzed transesterification (step 2) with material and enthalpy balance

to the process was unrecovered and was lost in waste water stream (stream 21). Glycerol was recovered by distillation in column C-4. Also ca. 5% of the WVO fed to the process was recovered in stream 23 as unconverted oil which can possibly be recycled to the process. About 2.3% of the biodiesel produced in reactor R-1 was lost through downstream biodiesel refining processes.

The energy requirements for major process equipment are summarized in table 1 and show that distillation columns require more energy than other equipment. As no heat integration opportunity was considered, only positive duties were considered as energy required. Therefore, the reboiler duty was taken as the energy required for a distillation column. 2.75 MJ are required to produce 1 Kg of biodiesel from WVO. The distribution of the process energy requirements is presented in fig. 3. Feed preparation and biodiesel production reaction only account for 3% of the energy required. Ethanol recovery (first and second step recovery) accounts for ca. 64% of the process energy requirements. Biodiesel refining by distillation accounts for ca. 27% of the total process energy requirements. The process also includes glycerol recovery which accounts for 3% process energy requirements. This step is useful as it will produce concentrated glycerol that can be sold to improve the process economics.

Table 1. Energy requirements for major process units in step 1 (fig. 1) and step 2 (fig. 2)

Equipment ID	Description	Energy required [MJ/h]	Equipment ID	Description	Energy required [MJ/h]
P-1	Pump (WVO feed)	0.1543	P-6	Pump (EtOH recycle)	0.0533
P-2	Pump (EtOH/H <sub>2</sub> SO <sub>4</sub> feed)	0.0154	P-7	Pump (Extractor column feed)	0.1911
E-1	Heat exchanger (feed pre-heater)	21.7843	E-3	Heat exchanger (feed pre-heater)	281.6053
R -1	Reactor (FFA esterification)	-7.1461	W-2	Washing column	-
R -2	Reactor (Neutralizer)	-507.4002	S-2	Gravity separator	-
S-1	Gravity separator	-	R -4	Reactor (Neutralizer)	79.2015
W-1	Washing column	-	S-3	Gravity separator	-
C-1	Distillation column (1st EtOH recovery) <i>35 stages, reflux ratio: 0.8638</i>		C-3	Distillation column (FAEE refining) <i>40 stages, reflux ratio: 0.015</i>	
	Condenser	-540.6249		Condenser	-416.2593
	Reboiler	528.079		Reboiler	674.968
P-3	Pump (EtOH recycle)	0.0945	C-4	Distillation column (Glycerol refining) <i>23 stages, reflux ratio: 0.002</i>	
P-4	Pump (Triolein feed)	0.0799		Condenser	-36.0485
				Reboiler	79
P-5	Pump (EtOH/NaOH feed)	0.0226			
E-2	Heat exchanger (feed pre-heater)	46.8967			
R -3	Reactor (Transesterification)	-313.8117			
C-2	Distillation column (2nd EtOH recovery) <i>43 stages, reflux ratio: 4.6465</i>				
	Condenser	-884.8256			
	Reboiler	1104.65			
<b>Total</b>					<b>2816.80*</b>
Biodiesel production [kg/h]					1026.1
<b>Energy requirement in MJ/kg biodiesel</b>					<b>2.75</b>

\* equal to the sum of positive duties

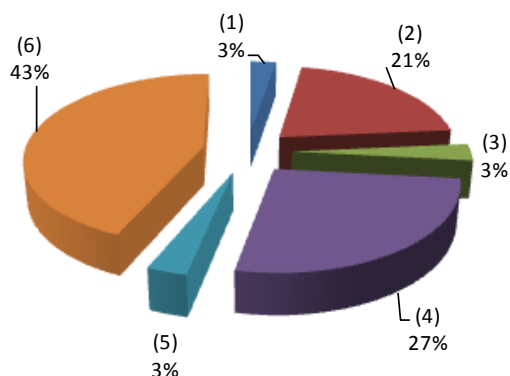


Fig. 3 Energy requirement distribution by process step: (1): Feed preparation and esterification + transesterification; (2): First step ethanol recovery and recycle; (3): Neutralization; (4): FAEE refining; (5): Glycerol recovery; (6): Second step ethanol recovery

## Conclusion

The energy required by the process of producing biodiesel from WVO and ethanol in a two step process using an homogenous acid catalyzed pre-treatment followed by a homogenous alkali catalyzed transesterification has been estimated by performing a process flowsheet simulation in ChemCad. With no attempt on process energy integration, the energy required to produce 1 kg of biodiesel was estimated as 2.75 MJ. Ethanol recovery accounts for the highest portion of the process energy requirements at 64% followed by biodiesel refining which accounts for 27% of the energy required for the process. The feed preparation and reaction accounted for 3% and glycerol recovery by distillation for 3% of the total energy required by the process.

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