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

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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

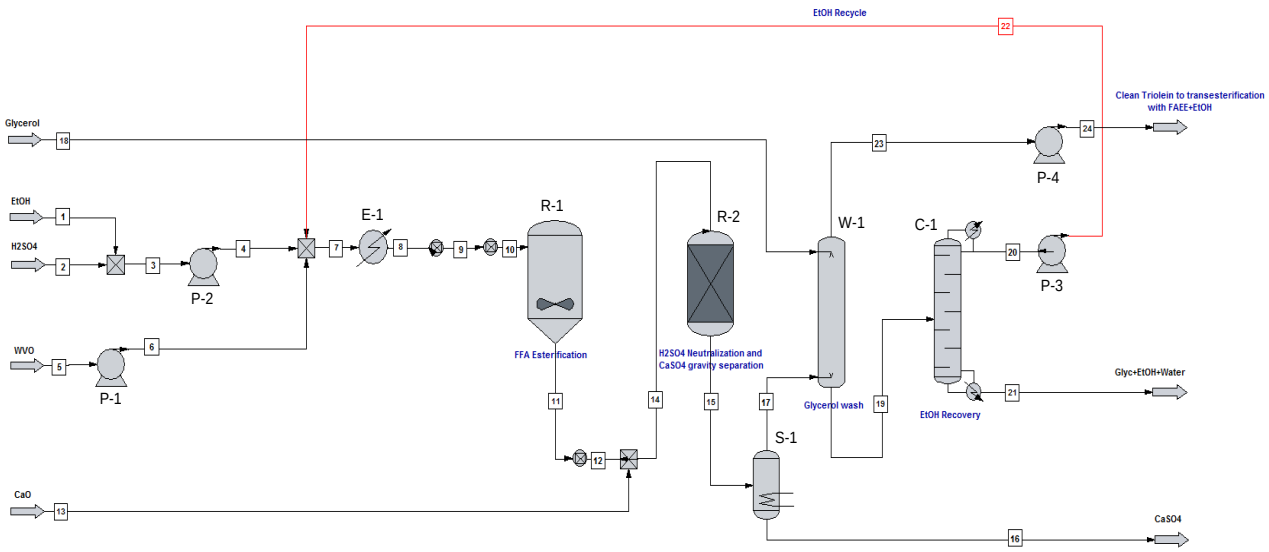
A process feed of 1050 kg/h of WVO was used for the process simulation and was modeled by a mixture of triolein (94 wt.%) and oleic acid (6 wt.%). Biodiesel was modeled by ethyl oleate and was referred to as fatty acid ethyl esters (FAEE). As this component was not available in the ChemCad component 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 colunms (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. Etanol and H_2SO_4 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_2SO_4 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_3PO_4 (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 x R_{min} and 1.2 x 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.

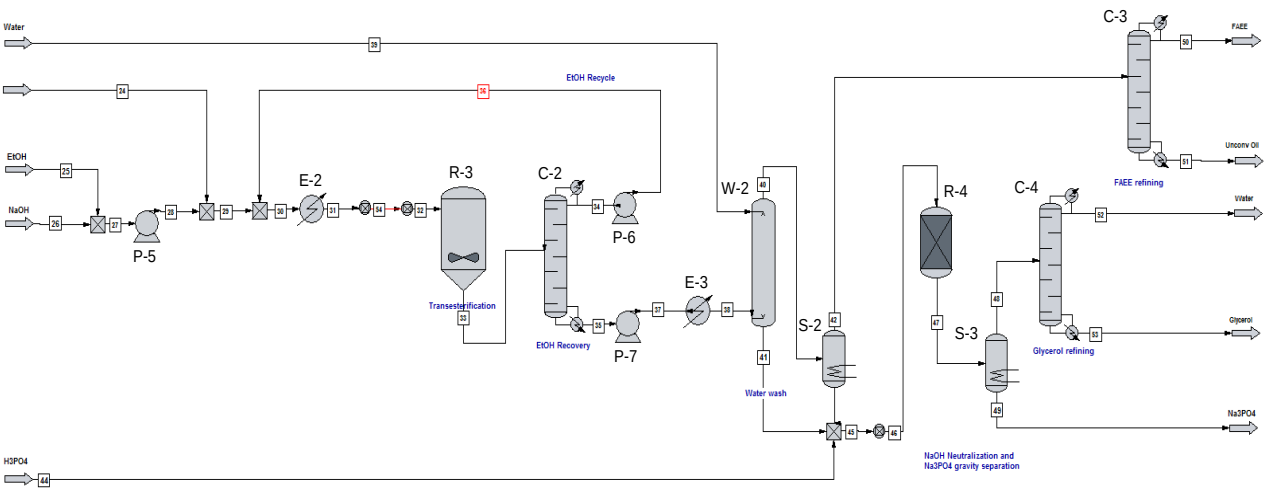
Results and discussion

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



Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Temperature [°C]	25.0	25.0	25.0	25.1	25.0	26.2	36.9	55.0	55.0	55.0	55.0	55.0	25.0	54.7	60.0	60.0	60.0	25.0	57.0	42.0	56.8	42.1	36.5	36.9
Pressure [kPa]	100	100	100	200	100	200	200	200	200	200	200	200	200	200	200	200	200	200	160	20	30	200	150	200
Enthalpy [MJ/h]	-488.73	-176.54	-665.27	-665.26	-2265.4	-2265.3	-4860.4	-4838.6	-4838.6	-4838.6	-4845.7	-4845.7	290.26	-4555.5	-5062.9	-335.26	-4727.6	-725.04	-3075.9	-1929.9	-1158.5	-1929.8	-2376.8	-2376.7
Flowrates [kg/h]																								
Ethyl Oleate											65.794	65.794		65.794	65.794		65.794		1.575		1.575		64.218	64.218
Ethanol	81.147		81.147	81.147			375.943	375.943	375.943	375.943	366.182	366.182		366.182	366.182		366.182		347.635	294.796	52.839	294.796	18.547	18.547
triolein					987.000	987.000	987.000	987.000	987.000	987.000	987.000	987.000		987.000	987.000		987.000		0.022		0.022		986.978	986.978
Glycerol																		100.000	99.923		99.923		0.078	0.078
Oleic Acid					63.000	63.000	63.000	63.000	63.000	63.000	3.150	3.150		3.150	3.150		3.150		0.331		0.331		2.820	2.820
Water							10.578	10.578	10.578	10.578	14.395	14.395		14.395	18.445		18.445		18.408	10.578	7.830	10.578	0.037	0.037
H2SO4		22.050	22.050	22.050			22.050	22.050	22.050	22.050	22.050	22.050		22.050										
CaO													12.607	12.607										
CaSO4															30.607	30.607								
Sodium Hydroxide																								
Phosphoric Acid																								
TriNa Phosphate																								

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



Stream No.	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Temperature [°C]	36.9	25.0	25.0	25.0	25.1	29.5	29.3	75.0	75.0	75.0	29.1	154.3	29.2	154.3	60.0	25.0	59.3	60.0	59.3	59.3	25.0	58.3	58.3	5.0	5.0	5.0	154.7	186.4	59.6	151.8	75.0
Pressure [kPa]	200	100	100	100	200	200	200	200	200	200	10	20	200	110	110	110	110	120	110	110	200	110	110	110	110	110	20	30	20	30	200
Enthalpy [MJ/h]	-2376.7	-771.05	-249.08	-1020.1	-1020.1	-3396.9	-4424	-4377.1	-4377.1	-4690.1	-1027.2	-3443.1	-1027.2	-3442.9	-3724.6	-174.45	-3004.4	-894.53	-2777.6	-226.8	-138.04	-1259.4	-1259.4	-1180.2	-977.16	-203.01	-2347.1	-163.56	-235.46	-698.73	-4377.1
Flowrates [kg/h]																															
Ethyl Oleate	64.218					64.218	64.226	64.226	64.226	1050.671	0.008	1050.663	0.008	1050.663	1050.663		1050.661	0.002	1050.661			0.002	0.002	0.002	0.002		1026.129	24.532	0.002		64.226
Ethanol	18.547	128.023		128.023	128.023	146.570	308.422	308.422	308.422	161.919	161.852	0.067	161.852	0.067	0.067		0.033	0.023		0.033		0.056	0.056	0.056	0.056				0.056		308.422
triolein	986.978					986.978	986.978	986.978	986.978	49.349		49.349		49.349	49.349		49.349	0.000	49.349			0.000			0.000		0.748	48.601			986.978
Glycerol	0.078					0.078	0.078	0.078	0.078	97.602		97.602		97.602	97.602		0.000	97.602				97.602	97.602	97.602	97.602				0.007	97.594	0.078
Oleic Acid	2.820					2.820	2.820	2.820	2.820	2.820		2.820		2.820	2.820		2.819		2.819						0.000		0.005	2.814			2.820
Water	0.037					0.037	3.446	3.446	3.446	3.450	3.409	0.041	3.409	0.041	0.041	11.000	3.742	7.296		3.742		11.038	11.038	16.595	16.595				14.960	1.634	3.446
H2SO4																															
CaO																															
CaSO4																															
Sodium Hydroxide			12.337	12.337	12.337	12.337	12.337	12.337	12.337	12.337		12.337		12.337	12.337		8.333	4.004		8.333		12.337	12.337								12.337
Phosphoric Acid																					10.076	10.076	10.076								
TriNa Phosphate																								16.856		16.856					

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_2SO_4 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)		C-3	Distillation column (FAEE refining)	
	35 stages, reflux ratio: 0.8638			*40 stages, reflux ratio: 0.015*	
	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)	
P-4	Pump (Triolein feed)	0.0799		*23 stages, reflux ratio: 0.002*	
				Condenser	-36.0485
P-5	Pump (EtOH/NaOH feed)	0.0226		Reboiler	79
E-2	Heat exchanger (feed pre-heater)	46.8967			
R -3	Reactor (Transesterification)	-313.8117			
C-2	Distillation column (2nd EtOH recovery)				
	43 stages, reflux ratio: 4.6465				
	Condenser	-884.8256			
	Reboiler	1104.65			

Total	**2816.80***
Biodiesel production [kg/h]	1026.1
Energy requirement in MJ/kg biodiesel	**2.75**

* equal to the sum of positive duties

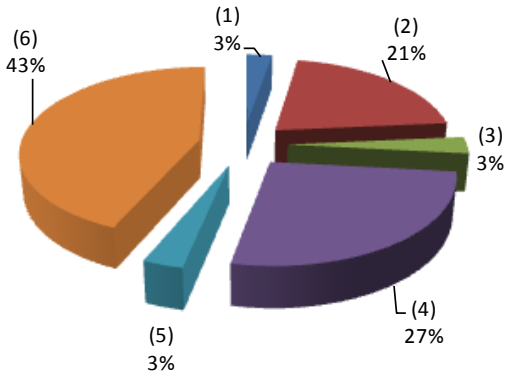


Fig. 3 Energy requirement distribution by process step: (1): Feed preparation and esterification + transesterification; (2): First step ethanol recovery and recycle; (3): Neutralization; (4): FAEE refining; (5): Glycerol recovery; (6): Second step ethanol recovery

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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