Simulation of a Continuous Process for Biodiesel Synthesis from Triacylglycerol based on Different Topologies

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Biodiesel is one of the two liquid biofuels that on short term is expected to contribute to reduce dependence on fossil fuels for transportation. Today biodiesel is a competitive and high developed commercial product in the European fuel market, using the broadest range of raw materials both from North to South Europe. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, essentially free of sulphur and aromatics, reducing substantially carbon footprint. Vegetable oils can be used straight as biofuel or can be turned into biodiesel by chemical process (transesterification) (Chang and Liu, 2010, Bambase et al., 2007, Noureddini and Zhu, 1997). Fatty acid distribution in common oils used for biodiesel production is given in Table 1.

1. Transesterification reaction
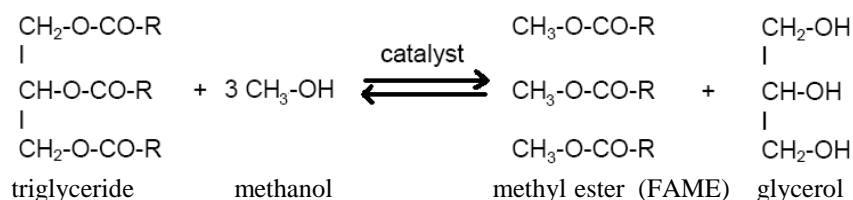
The reaction occurs under basic catalysis, acid catalysis or in supercritical methanol. Typical reaction conditions for each case (Al-Zuhair, 2007), are presented in Table 2.

Table 1: Fatty acid distribution of common biodiesel feedstocks [Lee et al, 2009 and Navarez et al, 2007)

Oil type	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0 C22:0
Soybean	0.3	7-11	0-1	3-6	22-34	50-60	2-10	5-10
Palm	1-6	32-47	-	1-6	40-52	2-11	-	-
Corn	1-2	8-12	-	2-5	19-49	34-52	-	-
Peanuts	-	8-9	-	2-3	50-60	20-30	-	-
Flaxseed	-	4-7	-	2-4	25-40	35-40	25-60	-

2. Physical properties

2.1 Physical properties of pure components

Usual simulator databases do not contain all components of interest in biodiesel synthesis. In this work it is described the development of component database for ProSimPlus 3.1 process simulator from ProSim. To estimate pure component physical properties for biodiesel and vegetable oils components ICAS-ProPred software (CAPEC, 2010) used with Marrero and Gani group contribution method. Some properties are constant with respect to temperature (critical temperature, pressure, and volume, molecular weight, etc.) while others vary with temperature (density, viscosity, heat capacity, vapour pressure, etc). The results may be manually transferred in ProSimPlus 3.1, using Component Plus software (Prosim, 2010).

2.2 Physical properties for binary and ternary mixtures

Once created, database can be used in SIMULIS to predict binary and ternary mixtures physical properties. Since the system contains polar components (such as methanol and glycerol), which imply strong interactions in liquid phase, and the operating pressure is low (from 0.1 to 4 bars), to create the binary and ternary phase diagrams UNIFAC modified (Dortmund) 1993 is used for liquid phase, while vapour phase model is ideal gas. In Figure 1 a ternary mixture phase diagram is presented.

Table 2: Comparisons between methods to obtain biodiesel (Al-Zuhair, 2007)

	Alkali catalyst	Acid catalyst	Supercritical methanol
Reaction temperature, K	303-338	338	523-573
Reaction pressure, MPa	0.1	0.1	10-25
Reaction time, min	60-360	4140	7-15
Methyl ester yield, wt%	96	90	98

Figure 1 provides information about the system methanol-methyl oleate-glycerol, i.e. the components obtained after transesterification reaction, if excess methanol is used:
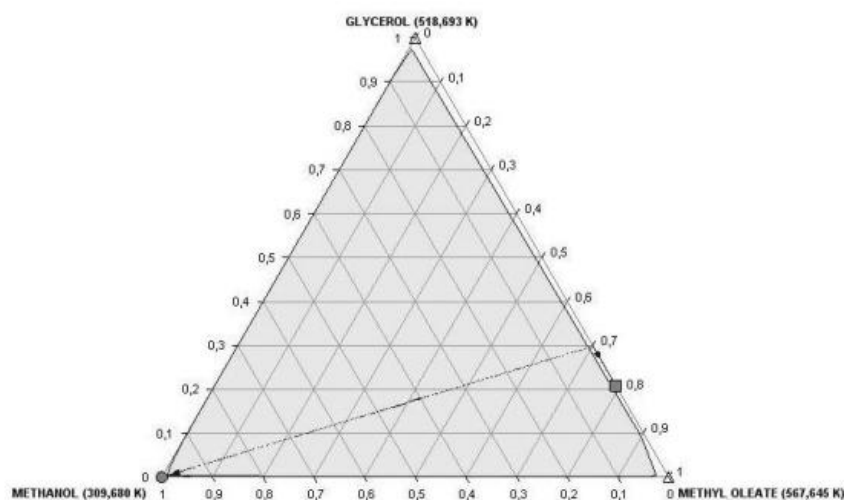
Figure 1 Ternary diagram of glycerol-methanol-methyl oleate system

(1) The system is biphasic for a wide range of compositions (shaded area), so the products can be separated using a decanter.

(2) Methanol vertex is an unstable point, so methanol can be separated by distillation and recycled into the reactor.

From information above, two topologies for biodiesel plant are considered in this paper:

(i) to separate glycerol-FAME system using a decanter, then to separate methanol from both mixtures using 2 distillation columns and then to recycle it;

(ii) to separate methanol by distillation and to recycle it; then to separate methyl esters-glycerol system using a decanter. These topologies are implemented in ProSimPlus 3.1.

3. Decanter-column topology

3.1 Process feed

Methanol stream flowrate is 19.9527 kmol/h. Trioleine stream flowrate is 6.9999 kmol/h. Catalyst (NaOH) feed flowrate is 1.5 kmol/h. Phosphoric acid (H_3PO_4) feed flowrate is 0.5 kmol/h. All this streams have temperature 70^0C, and pressure 1 atm.

3.2 Reactors

There are 2 reactors, one for transesterification reaction and the other for alkali catalyst neutralisation with phosphoric acid. Transesterification reactor is a CSTR, with kinetics given in Table 3. Residence time is considered 1 hour. For the neutralisation rector, conversion is 1, with respect to alkali catalyst. Both reactors are isothermal and no pressure drop is considered.

3.3 Distillation columns

The column used for separating methanol/methyl ester system has 3 stages and the feed is on second stage. The specifications for this column are: vapour distillate flowrate is

1360

3.8 kgmoles/h and molar reflux flowrate is 1 kmol/h. Meeting these specifications, the residue should contain 0.0001 mole fraction methanol.
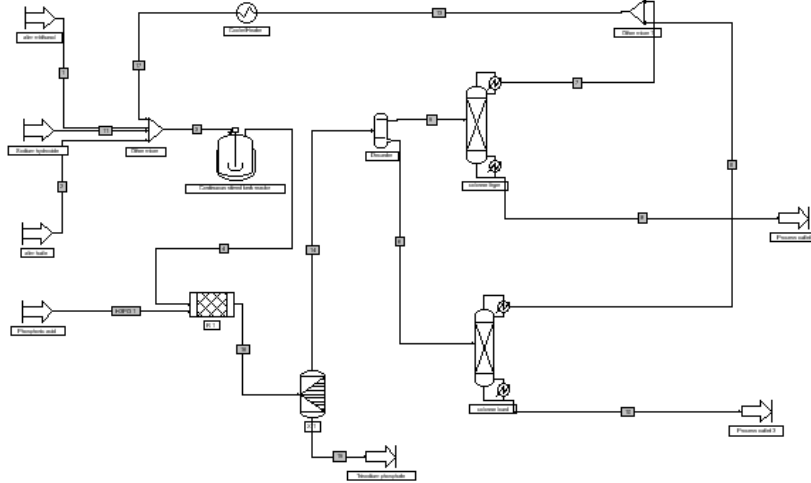

Figure 2: Biodiesel plant flowsheet using decanter-column topology

The column used to separate glycerol has five stages with feed on second stage. Vapour distillate flowrate is 9 kgmoles/h and molar reflux flowrate is 7.89 kgmoles/h. Consequently, residue methanol mole fraction is 0.0001 (Darnoko and Kerian, 2000).

4. Column-decanter topology

4.1 Process feed and reactors
Process feed and reactors data are the same as the data for decanter-column topology.

Table 3: Kinetic parameters for transesterification (Slinn and Kendall, 2009)

Reaction	Pre-exponential factor $(L^2/(mol^2*min))$	Activation Energy (J/mol)
Trigliceride-digliceride	$3.5093*10^{12}$	$7.2963*10^4$
Digliceride-trigliceride	$1.1542*10^{13}$	$7.1648*10^4$
Digliceride-monogliceride	$4.9432*10^{17}$	$9.7825*10^4$
Monogliceride-digliceride	$1.2895*10^{17}$	$9.4770*10^4$
monogliceride-glicerol	$6.2713*10^2$	$1.2020*10^4$

4.2 Distillation columns
The column used for separating methanol has 5 stages and the feed is on second stage. Column specifications are: liquid distillate flowrate is 8.499 kgmoles/h and molar reflux ratio is 4. Consequently recovery ratio of methanol in liquid distillate is 0.9258 molar is

obtained. The column used to separate glycerol has 10 stages and the feed is on 5th stage. Column specifications to obtain a good glycerol separation are: vapour distillate flowrate 0.4 kgmoles/h and molar reflux ratio 0.4.
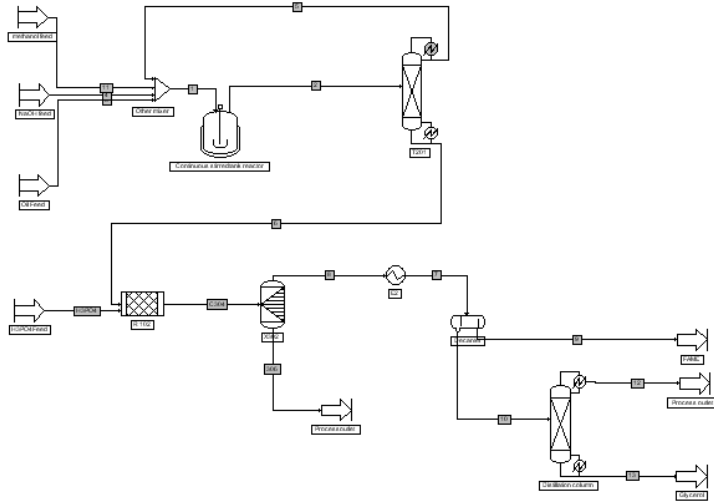

Figure 3: Biodiesel plant flowsheet using column-decanter topology

5. Assess Environmental Impact using Waste Reduction Algorithm (WAR) Software Tool

Introducing the input and output data form both topologies in WAR software (EPA, 2010) the results given in Figure 4 are obtained.
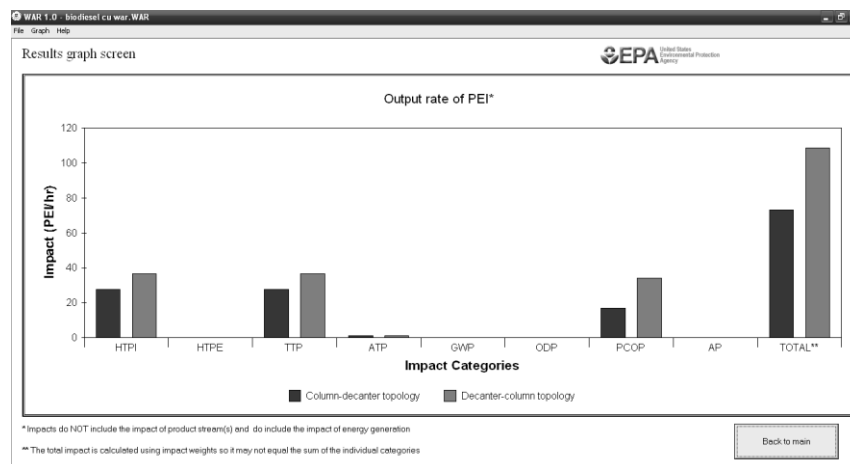

Figure 4: Assess Environmental Impact using WAR

6. Results and conclusions

Simulating both topologies in ProSimPlus 3.1, following results are obtained.

6.1 Decanter-column topology
Methyl ester rich stream contains 0.9992 mole fraction methyl ester, 0.0007 mole fraction glycerol, 0.0001 mole fraction methanol. Glycerol rich stream contains 0.9997 mole fraction glycerol, 0.0001 methyl ester and 0.0001 mole fraction methanol.

6.2 Column-decanter topology
Methyl ester rich stream contains 0.909 mole fraction methyl ester, 0.068 mole fraction methanol and 0.022 mole fraction water. Glycerol rich stream contains 0.973 mole fraction glycerol, 0.07 mole fraction methanol and 0.019 mole fraction water.

6.3 Environmental point of view
Figure 4 shows that column-decanter topology provides a lower environmental impact to the environment per different categories and per total.

ProSimPlus 3.1 combined with ICAS environment allowed biodiesel synthesis processes simulation with kinetic data from literature. Different alternative topologies are quantitatively evaluated with WAR algorithm, showing which topology is the best.

Acknowledgements

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