Aspen Plus

Aspen Plus Biodiesel Model

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Revision History

Version	Description
V7.0	First version
V7.3	Revised model based on biodiesel databank with full speciation of biodiesel and kinetic model for transesterification.
V7.3.2	Update TC, PC, VC and OMEGA for tri-/di-/mono-glycerides
V8.2	Upgrade to V8.2
V8.4	Upgrade to V8.4
V8.6	Upgrade to V8.6
V9	Update electrolyte components to behave better when this model is extended.

Contents

Introduction

This example is a model of a process for the alkali catalyzed production of biodiesel from vegetable oil. It is intended to:

- Provide an example of how to model the different areas of this process
- Supply a starting set of components and physical property parameters for modeling processes of this type

The model is not intended for equipment design or for specifying other engineering documents without further review by a process engineer with experience of biodiesel processes.

The model includes:

- A nominal set of chemical species and property parameters for this process
- Typical process areas including: transesterification, methanol recovery, water washing, FAME purification, catalyst removal, glycerol purification, feed stock recovery and the main streams connecting these units
- Reaction kinetics of transesterification
- Key process control specifications such as pure methanol flow rate, phosphoric acid flow rate, and specifications for distillation columns

This model is an extension of an earlier biodiesel model in Aspen Plus examples. The previous model used a single triolein to represent the vegetable oil and a single fatty acid methyl ester to represent biodiesel product. A 95% conversion of feedstock is assumed to model the transesterification reaction. The earlier model provided a useful description of the biodiesel production process and a preliminary comparison of process parameters and modifications for biodiesel production when the constituent components of vegetable oils are not available.

The current model takes advantage of the new biodiesel databank which offers physical properties of triglycerides, diglycerides and monoglycerides. This new model has a detailed kinetic model for transesterification and it can be used to compare plant performance for various feedstocks. Moreover, the quality of biodiesels from different feedstocks, as measured by properties such as density and kinematic viscosity, can be evaluated according to the predicted composition profile of methyl fatty acid esters. The distribution of various byproducts and products can be linked to cost data for calculating the material costs from various feedstocks.

1 Components

The following components represent the chemical species present in the process:

Table 1. Components Used in the Biodiesel Model

ID	Type	Name	Formula
METHANOL	CONV	METHANOL	CH4O
OOO	CONV	TRIOLEIN	C57H104O6
MMM	CONV	TRIMYRISTIN	C45H86O6
PPP	CONV	TRIPALMITIN	C51H98O6
PPS	CONV	TAG-PPS	C53H102O6-13
PPO	CONV	TAG-POP	C53H100O6-5
POS	CONV	TAG-POS	C55H104O6-3
MMP	CONV	TAG-MMP	C47H90O6-10
PPLI	CONV	TAG-PLIP	C53H98O6-5
POO	CONV	TAG-POO	C55H102O6-6
PLIO	CONV	TAG-PLIO	C55H100O6-7
OOS	CONV	TAG-OOS	C57H106O6-4
OOLI	CONV	TAG-OOLI	C57H102O6-5
MPLI	CONV	TAG-MLIP	C51H94O6-3
MM	CONV	1,3-DIMYRISTIN	C31H60O5-1
PP	CONV	1,3-DIPALMITIN	C35H68O5-1
OO	CONV	1,3-DIOLEIN	C39H72O5-1
PO	CONV	SN-1-PALMITO-3-OLEIN	C37H70O5-3
PLI	CONV	SN-1-PALMITO-3-LINOLEIN	C37H68O5-3
MP	CONV	SN-1-MYRISTO-3-PALMITIN	C33H64O5-7
PS	CONV	SN-1-PALMITO-3-STEARIN	C37H72O5-7
OS	CONV	SN-1-OLEO-3-STEARIN	C39H74O5-4
LIO	CONV	SN-1-LINOLEO-3-OLEIN	C39H70O5-8
MLI	CONV	SN-1-MYRISTO-3-LINOLEIN	C35H64O5-3
1-M	CONV	1-MONOMYRISTIN	C17H34O4
1-P	CONV	1-MONOPALMITIN	C19H38O4
1-S	CONV	1-MONOSTEARIN	C21H42O4

ID	Type	Name	Formula
1-O	CONV	MONOOLEIN	C21H40O4
1-LI	CONV	1-MONOLINOLEIN	C21H38O4-1
METHYL-O	CONV	METHYL-OLEATE	C19H36O2
METHYL-P	CONV	METHYL-PALMITATE	C17H34O2-N1
METHYL-M	CONV	METHYL-MYRISTATE	C15H30O2-N1
METHYL-S	CONV	METHYL-STEARATE	C19H38O2-N1
METHY-LI	CONV	METHYL-LINOLEATE	C19H34O2
GLYCEROL	CONV	GLYCEROL	C3H8O3
NAOH	CONV	SODIUM-HYDROXIDE	NAOH
WATER	CONV	WATER	H2O
H3PO4	CONV	ORTHOPHOSPHORIC-ACID	H3PO4
NA3PO4	CONV	TRISODIUM-PHOSPHATE	NA3PO4

Vegetable oil is the mixture of triglycerides (TG) such as OOO, PPP and MMM, et al[1]. For this biodiesel model, we assume the feedstock is the palm oil whose composition profile is determined by Che Man[2]. Table 2 lists the glyceride composition of the refined, bleached and deodorized (RBD) palm oil.

Table 2. Glyceride Composition of RBD Palm Oil[2]

Glyceride	Glyceride Composition (%)
Diglyceride	**5.20**
Triglyceride	**94.80**
Triunsaturated	
OOO	4.40
OOLI	0.58
Total	**4.98**
Monosaturated	
PLIO	9.68
POO	23.26
OOS	2.24
Total	**35.18**
Disaturated	
MPLI	2.20
PPLI	9.23
PPO	29.62
POS	4.90
Total	**45.95**
Trisaturated	
MMM	0.42
MMP	1.70
PPP	5.51
PPS	1.06
Total	**8.69**

The detailed fatty acid distribution in diglycerides is not given, so for convenience, we represent all the diglycerides in the feed with the PP molecule.

Diglycerides (DG) such as MM, OO, PLi, MP and monoglycerides (MG) including 1-M, 1-P, 1-S, 1-O, 1-Li are the intermediates of the transesterification reaction.

Methyl-Oleate, Methyl-Palmitate, Methyl-Myristate, Methyl-Stearate, and Methyl-Linoleate are the biodiesel products, with glycerol as a by-product.

Sodium hydroxide is used as the catalyst, and is removed by adding H_3PO_4 to precipitate Na_3PO_4.

2 Process Description

The flowsheet is based upon information included in the paper of Zhang et al (2003)[3].

This biodiesel process model includes the following units:

Table 3. General Unit Operations Used in the Bio-Diesel Process

Unit	Purpose
Transesterification	React oil with alcohol in the presence of catalyst to yield biodiesel and glycerol
Methanol Recovery	Recover excess methanol
Water Washing	Separate fatty acid methyl ester (FAME) from glycerol and electrolytes
FAME Purification	Purify FAME and recover oil
Catalyst Removal	Remove excess catalyst
Glycerol Purification	Purify glycerol

3 Physical Properties

The models used to calculate physical properties in Aspen Plus are grouped into methods named after the central model, for example Ideal, Redlich-Kwong-Soave, and NRTL (Non-Random Two Liquid). The property method used in this biodiesel model is Dortmund modified UNIFAC. This is suitable for preliminary work. NRTL would probably give more accurate results, but requires estimation of NRTL binary interaction parameters.

Thermophysical property model parameters of tri-, di-, and mono-glycerides are currently available in the new biodiesel databank. It includes vapor pressure, heat of vaporization, ideal gas heat of formation, ideal gas heat capacity, liquid heat capacity, liquid molar volume and liquid viscosity. The detailed information for the development of these thermophysical property models has been presented in the literature[4-6]. In addition, the required TC, PC and OMEGA for Redlich-Kwong-Soave EOS used to model vapor phase properties is estimated with the Gani group contribution method.

4 Reactions

A kinetic reaction model named PALM-OIL has been created for use in REACTOR. In addition, catalyst removal is modeled with a fixed conversion reaction in NEUTR. (See Chapters 5 and 6 for more info on these blocks.)

A. Transesterification Kinetics: PALM-OIL

1. Kinetic OOO + Methanol --> Methyl-O + OO
2. Kinetic OO + Methyl-O --> OOO + Methanol
3. Kinetic OO + Methanol --> Methyl-O + 1-O
4. Kinetic Methyl-O + 1-O --> OO + Methanol
5. Kinetic 1-O + Methanol --> Glycerol + Methyl-O
6. Kinetic Glycerol + Methyl-O --> Methanol + 1-O

7. Kinetic MMM + Methanol --> Methyl-M + MM
8. Kinetic Methyl-M + MM --> MMM + Methanol
9. Kinetic MM + Methanol --> Methyl-M + 1-M
10. Kinetic Methyl-M + 1-M --> MM + Methanol
11. Kinetic 1-M + Methanol --> Glycerol + Methyl-M
12. Kinetic Glycerol + Methyl-M --> Methanol + 1-M

13. Kinetic PPP + Methanol --> Methyl-P + PP
14. Kinetic Methyl-P + PP --> PPP + Methanol
15. Kinetic PP + Methanol --> Methyl-P + 1-P
16. Kinetic Methyl-P + 1-P --> Methanol + PP
17. Kinetic 1-P + Methanol --> Glycerol + Methyl-P
18. Kinetic Glycerol + Methyl-P --> Methanol + 1-P

19. Kinetic PPS + Methanol --> Methyl-S + PP

20. Kinetic Methyl-S + PP --> PPS + Methanol
21. Kinetic PPS + Methanol --> Methyl-P + PS
22. Kinetic Methyl-P + PS --> PPS + Methanol
23. Kinetic PS + Methanol --> Methyl-P + 1-S
24. Kinetic Methyl-P + 1-S --> Methanol + PS
25. Kinetic 1-S + Methanol --> Glycerol + Methyl-S
26. Kinetic Glycerol + Methyl-S --> Methanol + 1-S
27. Kinetic PS + Methanol --> Methyl-S + 1-P
28. Kinetic Methyl-S + 1-P --> Methanol + PS

29. Kinetic PPO + Methanol --> Methyl-O + PP
30. Kinetic Methyl-O + PP --> PPO + Methanol
31. Kinetic PPO + Methanol --> Methyl-P + PO
32. Kinetic Methyl-P + PO --> PPO + Methanol
33. Kinetic PO + Methanol --> Methyl-P + 1-O
34. Kinetic Methyl-P + 1-O --> Methanol + PO
35. Kinetic PO + Methanol --> Methyl-O + 1-P
36. Kinetic Methyl-O + 1-P --> PO + Methanol

37. Kinetic MMP + Methanol --> Methyl-P + MM
38. Kinetic MM + Methyl-P --> Methanol + MMP
39. Kinetic MMP + Methanol --> Methyl-M + MP
40. Kinetic MP + Methyl-M --> Methanol + MMP
41. Kinetic MP + Methanol --> Methyl-P + 1-M
42. Kinetic Methyl-P + 1-M --> MP + Methanol
43. Kinetic MP + Methanol --> Methyl-M + 1-P
44. Kinetic Methyl-M + 1-P --> MP + Methanol

45. Kinetic PPLI + Methanol --> Methy-LI + PP
46. Kinetic Methy-LI + PP --> PPLI + Methanol
47. Kinetic PPLI + Methanol --> Methyl-P + PLI
48. Kinetic Methyl-P + PLI --> PPLI + Methanol
49. Kinetic PLI + Methanol --> Methy-LI + 1-P
50. Kinetic Methy-LI + 1-P --> PLI + Methanol
51. Kinetic PLI + Methanol --> Methyl-P + 1-LI
52. Kinetic Methyl-P + 1-LI --> PLI + Methanol

53. Kinetic 1-LI + Methanol --> Glycerol + Methy-LI
54. Kinetic Glycerol + Methy-LI --> Methanol + 1-LI

55. Kinetic POO + Methanol --> Methyl-O + PO
56. Kinetic Methyl-O + PO --> POO + Methanol
57. Kinetic POO + Methanol --> Methyl-P + OO
58. Kinetic Methyl-P + OO --> POO + Methanol

59. Kinetic POS + Methanol --> Methyl-S + PO
60. Kinetic Methyl-S + PO --> Methanol + POS
61. Kinetic POS + Methanol --> Methyl-P + OS
62. Kinetic Methyl-P + OS --> Methanol + POS
63. Kinetic POS + Methanol --> Methyl-O + PS
64. Kinetic Methyl-O + PS --> Methanol + POS

65. Kinetic PLIO + Methanol --> Methyl-O + PLI
66. Kinetic Methyl-O + PLI --> Methanol + PLIO
67. Kinetic PLIO + Methanol --> Methyl-P + LIO
68. Kinetic Methyl-P + LIO --> Methanol + PLIO
69. Kinetic PLIO + Methanol --> Methy-LI + PO
70. Kinetic Methy-LI + PO --> Methanol + PLIO
71. Kinetic LIO+ Methanol --> Methyl-O + 1-LI
72. Kinetic Methyl-O + 1-LI --> LIO + Methanol
73. Kinetic LIO+ Methanol --> Methy-LI + 1-O
74. Kinetic Methy-LI + 1-O --> LIO + Methanol

75. Kinetic OOS + Methanol --> Methyl-S + OO
76. Kinetic Methyl-S + OO --> OOS + Methanol
77. Kinetic OOS + Methanol --> Methyl-O + OS
78. Kinetic Methyl-O + OS --> OOS + Methanol
79. Kinetic OS + Methanol --> Methyl-O + 1-S
80. Kinetic Methyl-O + 1-S --> Methanol + OS
81. Kinetic OS + Methanol --> Methyl-S + 1-O
82. Kinetic Methyl-S + 1-O --> Methanol + OS

83. Kinetic OOLI + Methanol --> Methy-LI + OO

84. Kinetic Methy-LI + OO --> OOLI + Methanol
85. Kinetic OOLI + Methanol --> Methyl-O + LIO
86. Kinetic Methyl-O + LIO --> OOLI + Methanol

87. Kinetic MPLI + Methanol --> Methy-LI + MP
88. Kinetic Methy-LI + MP --> MPLI + Methanol
89. Kinetic MPLI + Methanol --> Methyl-M + PLI
90. Kinetic Methyl-M + PLI --> MPLI + Methanol
91. Kinetic MPLI + Methanol --> Methyl-P + MLI
92. Kinetic Methyl-P + MLI --> MPLI + Methanol
93. Kinetic MLI + Methanol --> Methyl-M + 1-LI
94. Kinetic Methyl-M + 1-LI --> MLI + Methanol
95. Kinetic MLI + Methanol --> Methy-LI + 1-M
96. Kinetic Methy-LI + 1-M --> MLI + Methanol

B. Catalyst Removal

3 NaOH + H_3PO_4 --> Na_3PO_4 + 3 Water 100% conversion of NaOH

The power expressions are used for the rate-controlled transesterification reactions:

$$r = k\left(\frac{T}{T_o}\right)^n \exp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i^{ai}\left(\frac{1}{T}-\frac{1}{T_o}\right) \quad (1)$$

Where:

r = Rate of reaction;

k = Pre-exponential factor;

T = Absolute temperature;

T_o = Reference temperature;

n = Temperature exponent;

E = Activation energy;

R = Universal gas constant;

N = Number of components in the reaction;

C_i = Concentration of component i;

a_i = The stoichiometric coefficient of component i in the reaction equation.

In equation (1), the concentration basis is Molarity, the factor n is zero, and k and E are given in Table 4. The kinetic parameters for reactions 1-96 in Table 4 are derived from the work of Narvaez et al. (2007)[7]. The effect of concentration of catalyst on the transesterification was studied in the paper[7], but the given kinetics didn't include the concentration of catalyst. So we made some conversions to add the concentration of catalyst (sodium hydroxide) into Narvaez's kinetics.

Table 4. Parameters k and E in Equation (1)

Reaction Type	Reaction No.	k (T_o =323.15K)	E (kcal/mol)
$TG \rightarrow DG$	1,7,13	0.02311	13.5
	19,29,37,45,57,59,61,63,65,67, 69,75,83,87,89,91	0.00770	
	21,31,39,47,55,77,85	0.01541	
$DG \rightarrow TG$	2,8,14,20,22,30,32,38,40,46, 48,56,58,60,62,64,66,68,70,76, 78,84,86,88,90,92	0.001867	10.3
$DG \rightarrow MG$	3,9,15	0.10659	17.4
	23,27,33,35,41,43,49,51,71,73, 79,81,93,95	0.05330	
$MG \rightarrow DG$	4,10,16,24,28,34,36,42,44,50, 52,72,74,80,82,94,96	0.002217	16.2
$MG \rightarrow FAME$	5,11,17,25,53	0.05754	6.2
$FAME \rightarrow MG$	6,12,18,26,54	0.000267	11.9

Note that Narvaez et al. (2007) just proposed the transesterification kinetics of palm oil instead of the individual triglycerides that make up the oil. So, in this work, we assume the kinetics of all the constituent triglycerides are the same as that for the triglyceride mixture, palm oil. For example, both reaction 1 and reaction 7 are steps to producing diglycerides (DG) from triglycerides (TG), so the rate constants of these two reactions are treated as equal. Another assumption is that we have considered all possible reactions for TGs and DGs. Using component PPS as the example:

PPS will take part in the following parallel reactions:

19. PPS + Methanol --> Methyl-S + PP

21. PPS + Methanol --> Methyl-P + PS

And the rate constant of Reaction 21 is regarded as twice that of Reaction 19 because there are two P fragments with PPS.

5 Simulation Approach

Unit Operations - Major unit operations in this model have been represented by Aspen Plus blocks as shown in Table 5.

Table 5. Aspen Plus Unit Operation Blocks Used in the Biodiesel Model

Unit Operation	Aspen Plus "Block"	Comments / Specifications
Transesterification	RCSTR	Rigorous simulation with kinetics reactions.
Methanol Recovery	RadFrac	Rigorous multi-stage distillation model. 7 theoretical stages.
Water Washing	Liquid-Liquid Extractor	Rigorous multi-stage liquid-liquid extractor model. 6 theoretical stages
FAME Purification	RadFrac	Rigorous multi-stage distillation model. 6 theoretical stages.
Catalyst Removal	RStoic Sep	Simplified simulation with stoichiometric reactions Simplified simulation for solid removal
Glycerol Purification	RadFrac	Rigorous multi-stage distillation model. 6 theoretical stages.

Streams - Streams represent the material and energy flows in and out of the process. Streams can be of three types: Material, Heat, and Work. Feeds to the biodiesel model are oil, methanol, sodium hydroxide, water and acid.

Design-Specs, Calculator Blocks - The simulation includes a Design Spec and a Calculator Block as shown in Tables 6 & 7:

Table 6. Design Specs Used in the Biodiesel Model

Spec Name	Spec (Target)	Manipulated Variable
MEOHCONC	Mass fraction of methanol in reactor outlet is 0.092	Methanol feed stream flow rate

Table 7. Flowsheet Calculators Used in the Biodiesel Model

Name	Purpose
PO3FLOW	H_3PO_4 feed flow is determined according to excess sodium hydroxide.

6 Simulation Results

The Aspen Plus simulation flowsheet is shown in Figure 1.

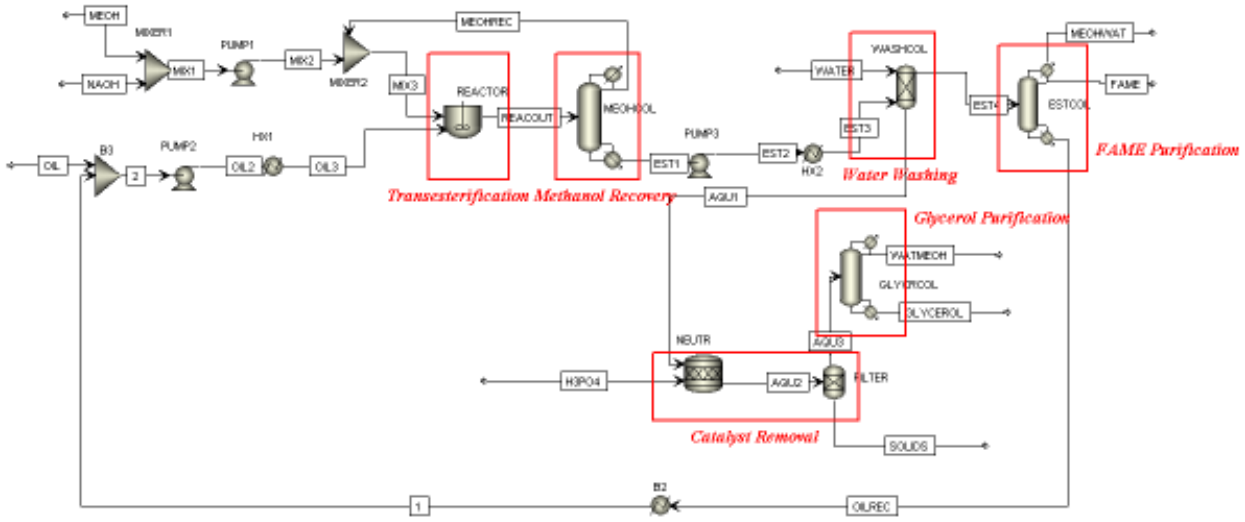

Figure 1. Biodiesel Flowsheet in Aspen Plus

Key simulation results are presented in Table 8.

Table 8. Key Simulation Results

Plant capacity (pure FAME)	9.19	MM kg/yr
Oil feed	1050	kg/hr
Methanol feed	127.1	kg/hr
Catalyst feed	50	kg/hr
H_3PO_4 feed	40.8	kg/hr
Water feed for washing	50	kg/hr
Transesterification reactor biodiesel composition	0.756	Mass fraction
Transesterification reactor oil conversion	0.980	1 h
Product FAME purity	0.997	Mass fraction
Product Glycerol purity	1	Mass fraction

The oil feed is the sum of the constituent triglycerides and diglycerides while the FAME production is the sum of all the methyl esters.

Table 9 compares the composition profile of biodiesel product calculated with the current model and with the previous model based on the same chemical feeds and flowsheet. The properties for biodiesel obtained in both simulations are analyzed to evaluate the quality specification required by ASTM (American Society for Testing and Materials)[8] and EN (European Norms) standards[9].

Table 9. FAME Distribution in the Product

	Current Model	Old Model	EN14214	ASTM D6751
Methyl-O (wt%)	37.82	99.7		
Methyl-P (wt%)	49.33	-		
Methyl-M (wt%)	2.15	-		
Methyl-S (wt%)	2.82	-		
Methyl-Li (wt%)	7.58	-		
FAME (wt%)	99.7	99.7	>96.5	
Monoglycerides (wt%)	0.27	-	<0.80	
Diglycerides (wt%)	Trace	-	<0.20	
Triglycerides (wt%)	Trace	0.3	<0.20	
Density at 15°C, kg/m3	873.6	874.7	860-900	

From the Table 9, the constituent FAMEs obtained in the two simulations are very different. So are the qualities of the biodiesel products. The new model offers the capability to model biodiesel product quality quantitatively.

Table 10 presents the composition profile of the recycled oil in both simulations.

Table 10. Composition of Recycled Oil

	Current Model	Old Model
Monoglycerides (wt%)	**35.2**	**-**
1-M	0.29	-
1-P	13.33	-
1-S	1.21	-
1-O	16.98	-
1-LI	3.37	-
Diglycerides (wt%)	**13.8**	**-**
MM	0.06	-
PP	3.35	-
OO	2.02	-
PO	5.51	-
PLI	1.09	-
MP	0.30	-
PS	0.37	-
OS	0.36	-
LIO	0.64	-
MLI	0.07	-

	Current Model	Old Model
Triglycerides (wt%)	**45.7**	**94.6**
OOO	2.28	94.6
MMM	0.18	-
PPP	3.33	-
PPS	0.61	-
PPO	14.82	-
POS	2.33	-
MMP	0.73	-
PPLI	4.35	-
POO	11.55	-
PLIO	2.84	-
OOS	1.05	-
OOLI	0.47	-
MPLI	0.97	-
FAMEs (wt%)	**5.3**	**5.4**
Total Flow (kg/h)	**41.57**	**54.91**

Figures 2 and 3 compare the temperature profiles in the glycerol purification column and FAME purification column, respectively.

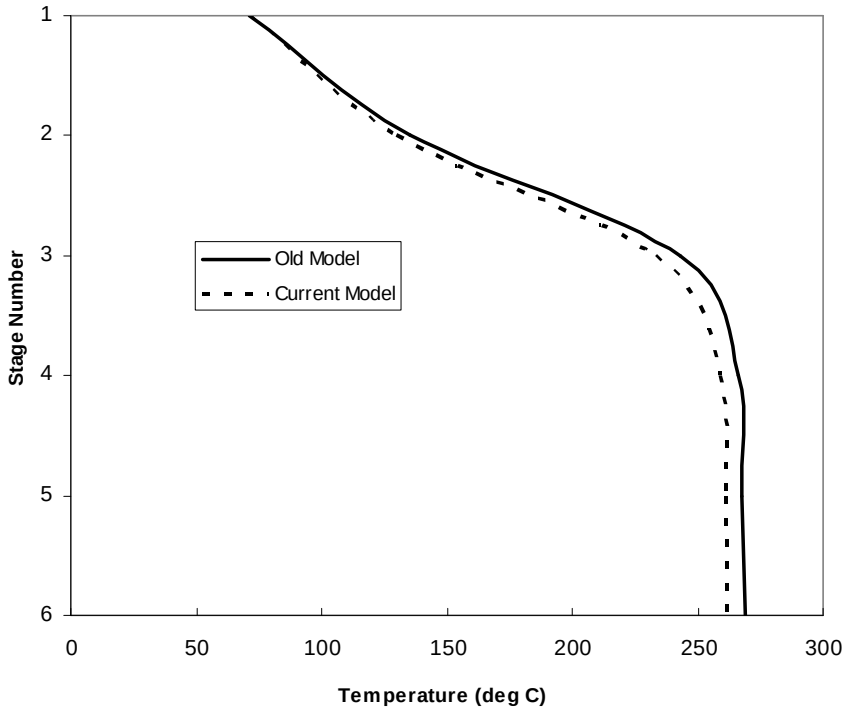

Figure 2. Glycerol Purification Temperature Profile for the Old Model and Current Model

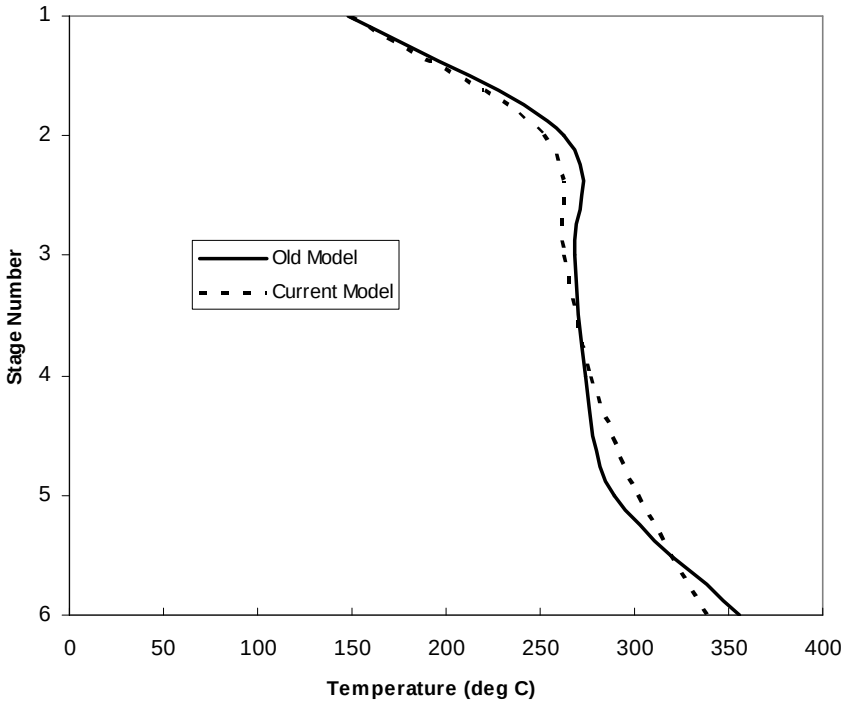

Figure 3. FAME Purification Temperature Profile for the Old Model and Current Model

7 Conclusions

The biodiesel model provides a useful description of the process, especially introducing the kinetics of transesterification into the process. The model can be used as a guide for understanding the process and the economics in change of biodiesel feedstock, and also as a starting point for more sophisticated models for plant design and specifying process equipment.

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