



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.

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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	CH ₄ O
OOO	CONV	TRIOLEIN	C ₅₇ H ₁₀₄ O ₆
MMM	CONV	TRIMYRISTIN	C ₄₅ H ₈₆ O ₆
PPP	CONV	TRIPALMITIN	C ₅₁ H ₉₈ O ₆
PPS	CONV	TAG-PPS	C ₅₃ H ₁₀₂ O ₆ -13
PPO	CONV	TAG-POP	C ₅₃ H ₁₀₀ O ₆ -5
POS	CONV	TAG-POS	C ₅₅ H ₁₀₄ O ₆ -3
MMP	CONV	TAG-MMP	C ₄₇ H ₉₀ O ₆ -10
PPLI	CONV	TAG-PLIP	C ₅₃ H ₉₈ O ₆ -5
POO	CONV	TAG-POO	C ₅₅ H ₁₀₂ O ₆ -6
PLIO	CONV	TAG-PLIO	C ₅₅ H ₁₀₀ O ₆ -7
OOS	CONV	TAG-OOS	C ₅₇ H ₁₀₆ O ₆ -4
OOLI	CONV	TAG-OOLI	C ₅₇ H ₁₀₂ O ₆ -5
MPLI	CONV	TAG-MLIP	C ₅₁ H ₉₄ O ₆ -3
MM	CONV	1,3-DIMYRISTIN	C ₃₁ H ₆₀ O ₅ -1
PP	CONV	1,3-DIPALMITIN	C ₃₅ H ₆₈ O ₅ -1
OO	CONV	1,3-DIOLEIN	C ₃₉ H ₇₂ O ₅ -1
PO	CONV	SN-1-PALMITO-3-OLEIN	C ₃₇ H ₇₀ O ₅ -3
PLI	CONV	SN-1-PALMITO-3-LINOLEIN	C ₃₇ H ₆₈ O ₅ -3
MP	CONV	SN-1-MYRISTO-3-PALMITIN	C ₃₃ H ₆₄ O ₅ -7
PS	CONV	SN-1-PALMITO-3-STEARIN	C ₃₇ H ₇₂ O ₅ -7
OS	CONV	SN-1-OLEO-3-STEARIN	C ₃₉ H ₇₄ O ₅ -4
LIO	CONV	SN-1-LINOLEO-3-OLEIN	C ₃₉ H ₇₀ O ₅ -8
MLI	CONV	SN-1-MYRISTO-3-LINOLEIN	C ₃₅ H ₆₄ O ₅ -3
1-M	CONV	1-MONOMYRISTIN	C ₁₇ H ₃₄ O ₄
1-P	CONV	1-MONOPALMITIN	C ₁₉ H ₃₈ O ₄
1-S	CONV	1-MONOSTEARIN	C ₂₁ H ₄₂ O ₄

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	WATER	H2O
WATER	CONV	WATER	H2O
H3PO4	CONV	WATER	H2O
NA3PO4	CONV	WATER	H2O

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 . Because electrolyte chemistry is not modeled in detail, these electrolytes are modeled using physical property data for water, but with their correct molecular weights.

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.

However, the Dortmund modified UNIFAC model requires the UFGRPD parameter. This parameter stores the functional group information which contains UNIFAC group numbers and the number of occurrences of each group. For those components missing the UFGRPD parameters, the Property Estimation tool in Aspen Plus, when enabled, can automatically calculate UFGRPD according to their molecular structures. Analogously, when the UNIFAC model or Lyngby modified UNIFAC model is used, UFGRP and UFGRPL parameters are required, respectively.

So for convenience, we select **Estimate all missing parameters** in Estimation options in this model.

Thermophysical property model parameters of tri-, di-, and mono-glycerides are currently available in the new biodiesel databank.

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 $\text{OOO} + \text{Methanol} \rightarrow \text{Methyl-O} + \text{OO}$
2. Kinetic $\text{OO} + \text{Methyl-O} \rightarrow \text{OOO} + \text{Methanol}$
3. Kinetic $\text{OO} + \text{Methanol} \rightarrow \text{Methyl-O} + \text{1-O}$
4. Kinetic $\text{Methyl-O} + \text{1-O} \rightarrow \text{OO} + \text{Methanol}$
5. Kinetic $\text{1-O} + \text{Methanol} \rightarrow \text{Glycerol} + \text{Methyl-O}$
6. Kinetic $\text{Glycerol} + \text{Methyl-O} \rightarrow \text{Methanol} + \text{1-O}$

7. Kinetic $\text{MMM} + \text{Methanol} \rightarrow \text{Methyl-M} + \text{MM}$
8. Kinetic $\text{Methyl-M} + \text{MM} \rightarrow \text{MMM} + \text{Methanol}$
9. Kinetic $\text{MM} + \text{Methanol} \rightarrow \text{Methyl-M} + \text{1-M}$
10. Kinetic $\text{Methyl-M} + \text{1-M} \rightarrow \text{MM} + \text{Methanol}$
11. Kinetic $\text{1-M} + \text{Methanol} \rightarrow \text{Glycerol} + \text{Methyl-M}$
12. Kinetic $\text{Glycerol} + \text{Methyl-M} \rightarrow \text{Methanol} + \text{1-M}$

13. Kinetic $\text{PPP} + \text{Methanol} \rightarrow \text{Methyl-P} + \text{PP}$
14. Kinetic $\text{Methyl-P} + \text{PP} \rightarrow \text{PPP} + \text{Methanol}$
15. Kinetic $\text{PP} + \text{Methanol} \rightarrow \text{Methyl-P} + \text{1-P}$
16. Kinetic $\text{Methyl-P} + \text{1-P} \rightarrow \text{Methanol} + \text{PP}$
17. Kinetic $\text{1-P} + \text{Methanol} \rightarrow \text{Glycerol} + \text{Methyl-P}$
18. Kinetic $\text{Glycerol} + \text{Methyl-P} \rightarrow \text{Methanol} + \text{1-P}$

19. Kinetic $\text{PPS} + \text{Methanol} \rightarrow \text{Methyl-S} + \text{PP}$

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

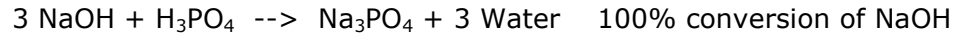
81. Kinetic OS + Methanol --> Methyl-S + 1-O

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



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

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

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.

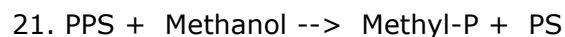
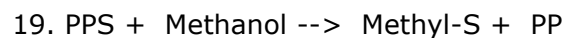
In equation (1), the concentration basis is Molarity, the factor n is zero, and k and E are given in Table 4. The kinetic parameters for reactions 1-96 in Table 4 are derived from the work of Narvaez et al. (2007)^[4]. The effect of concentration of catalyst on the transesterification was studied in the paper^[4], 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:



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 Approaches

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	Simplified simulation with stoichiometric reactions
	Sep	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 ₃ PO ₄ feed flow is determined according to excess sodium hydroxide.

6 Simulation Results

The Aspen Plus simulation flowsheet is shown in Figure 1.

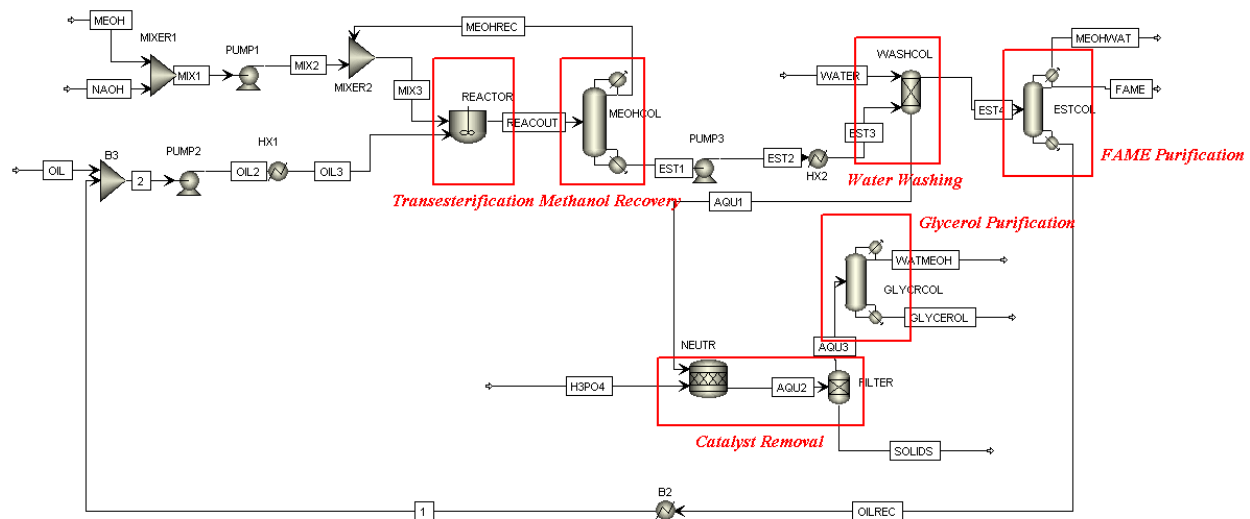


Figure 1. Biodiesel Flowsheet in Aspen Plus

Key simulation results are presented in Table 8.

Table 8. Key Simulation Results

Plant capacity (pure FAME)	9.23	MM kg/yr
Oil feed	1050	kg/hr
Methanol feed	127.094	kg/hr
Catalyst feed	50	kg/hr
H ₃ PO ₄ feed	40.8	kg/hr
Water feed for washing	50	kg/hr
Transesterification reactor biodiesel composition	0.758	Mass fraction
Transesterification reactor oil conversion	0.983	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 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)^[5] and EN (European Norms) standards^[6].

Table 9. FAME Distribution in the Product

	Current Model	Old Model	EN14214	ASTM D6751
Methyl-O (wt%)	37.82	99.7		
Methyl-P (wt%)	49.34	-		
Methyl-M (wt%)	2.15	-		
Methyl-S (wt%)	2.82	-		
Methyl-Li (wt%)	7.57	-		
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/m ³	889.19	874.7142	860-900	
Viscosity at 40°C, mm ² /s	3.85	4.54	3.50-5.00	1.90-6.00

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%)	35.3	-
1-M	0.27	-
1-P	12.76	-
1-S	1.25	-
1-O	17.55	-
1-LI	3.46	-
Diglycerides (wt%)	13.7	-
MM	0.06	-
PP	3.28	-
OO	2.03	-
PO	5.48	-
PLI	1.09	-
MP	0.30	-
PS	0.36	-
OS	0.36	-
LIO	0.64	-

	Current Model	Old Model
MLI	0.07	-
Triglycerides (wt%)	45.6	94.6
OOO	2.29	94.6
MMM	0.18	-
PPP	3.30	-
PPS	0.61	-
PPO	14.85	-
POS	2.34	-
MMP	0.74	-
PPLI	4.37	-
POO	11.60	-
PLIO	2.85	-
OOS	1.06	-
OOLI	0.46	-
MPLI	0.98	-
FAMEs (wt%)	5.4	5.4
Total Flow (kg/h)	38.36	54.91

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

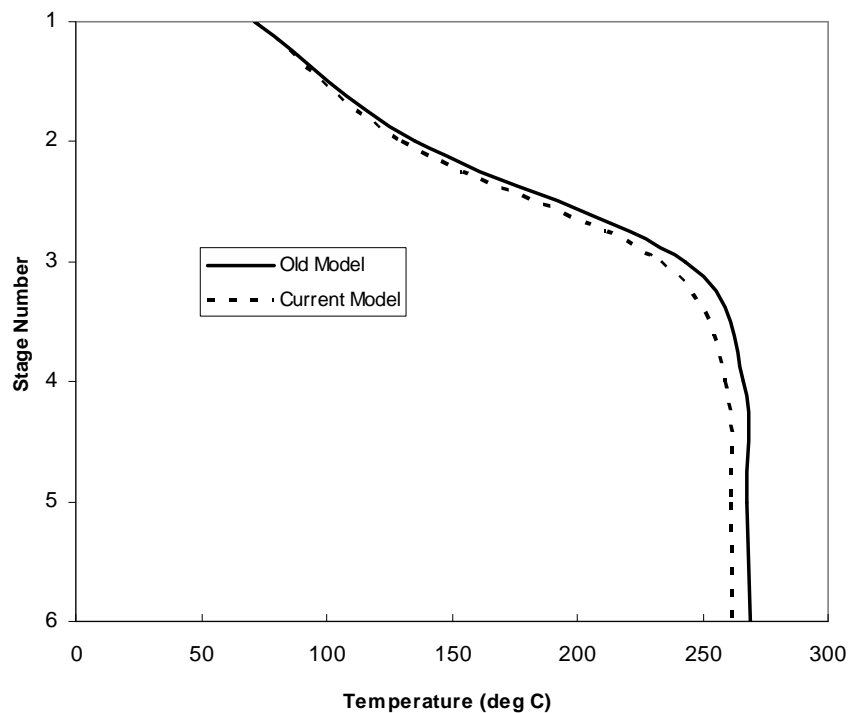


Figure 2. Glycerol Purification Temperature Profile for the Old Model and Current Model

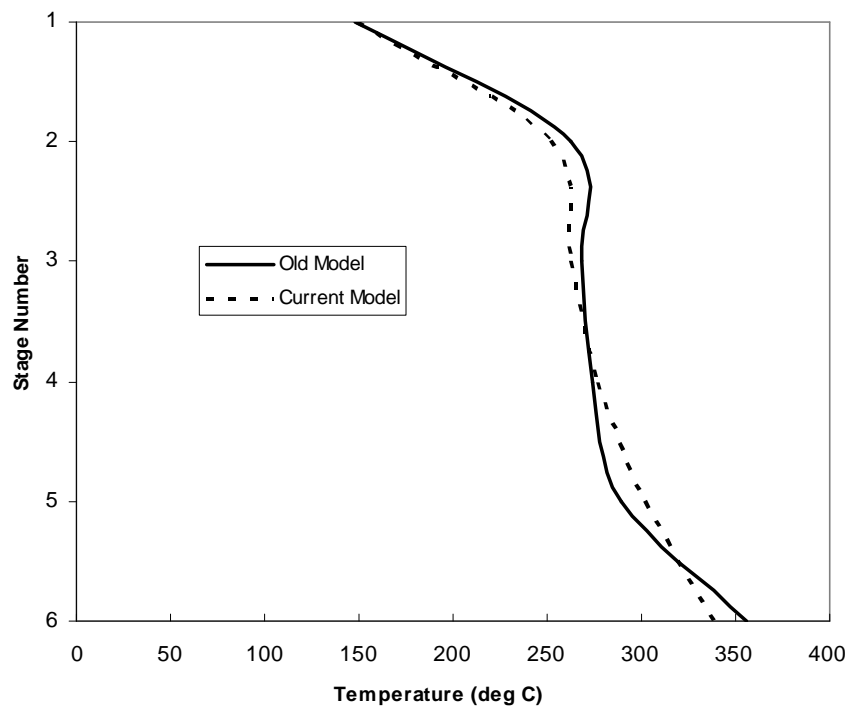


Figure 3. FAME Purification Temperature Profile for the Old Model and Current Model

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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