Supporting Information

Reactive distillation toward eco-efficient process of continuous biodiesel manufacture from waste oil: Pilot-scale experiments and process design

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Section 1. The kinetic parameter data.

Table S1. Kinetic constants of the reaction system at different temperatures.

Temperature (K)	$k*10^4/(L\cdot mol^{-1}\cdot min^{-1})$					
	k_{1+}	k_{1-}	k_{2+}	k_{2-}	k_{3+}	k_{3-}
341.15	69.13	45.54	594.95	239.09	23.73	18.81
336.15	51.31	39.55	472.43	195.74	14.07	11.47
331.15	42.73	36.26	410.03	173.10	10.21	8.47

Table S2. Estimated kinetic parameter values.

k_i	k_{0i} (L mol^{-1} s^{-1})	E_{ai} (kJ/mol)
k_{1-}	5.505×10^6	45.13
k_{1-}	62.483	21.38
k_{2+}	1.301×10^4	34.92
k_{2-}	0.103×10^4	30.29
k_{3+}	2.965×10^9	79.11
k_{3-}	5.367×10^9	94.91

Section 2. The detailed pilot-scale reactive distillation experimental results.

Table S3. The detailed pilot-scale reactive distillation experimental results.

Run number	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6
Experiment time(h)	0-18	18-34	34-47.5	47.5-59.5	59.5-72	72-88
Steady-state time(h)	14-18	31-34	43-47.5	56.5-59.5	67-72	86-88
Feeding position	1/4	1/4	1/4	1/4	1/4	1/1
Reflux ratio	1	1	1	0.5	0.1	1
F_{SODD}(g/h)	117.8	81.1	48.1	79.1	78.9	79.6
F_{MeOH}(g/h)	122.2	158.9	191.9	160.9	161.1	160.4
D(g/h)	115.2	142.3	168.4	146.3	148.7	142.3
B(g/h)	124.8	97.7	71.6	93.7	91.3	97.7
D/F (mass based)	0.48	0.59	0.70	0.60	0.61	0.59
Total feeding rate(g/h)	240	240	240	240	240	240
Mass ratio (MeOH/SODD)	1.04	1.96	3.99	2.03	2.04	2.02
FMR(MeOH/FFA)	16.75	31.56	64.24	32.68	32.84	32.52
X_D(MeOH)	0.9690	0.9887	0.9935	0.9879	0.9893	0.9917
X_D(water)	0.0189	0.0113	0.0065	0.0121	0.0107	0.0083
X_B(MeOH)	0.0082	0.0103	0.0112	0.0093	0.0081	0.0106
X_B(FFA)	0.2395	0.1935	0.1234	0.1619	0.1965	0.2533
Conversion of FFA(%)	53.35	57.14	66.23	64.75	58.21	42.855

Section 3. Physical parameters and thermodynamic data in simulation.

Table S4. UNIFAC model parameters of FFA esterification parameters.

Component i	Component j	A_{ij}	A_{ji}	B_{ij} (K)	B_{ji} (K)	Sources
C1	M1	0	0	43.45581	-55.4737	predict by UNIFAC
C1	water	0	0	-607.901	-205.828	predict by UNIFAC
C1	C2	0	0	104.078	-119.081	predict by UNIFAC
C1	M2	0	0	-19.3846	15.2478	predict by UNIFAC
C1	M3	0	0	74.63104	-100.406	predict by UNIFAC
MeOH	C2	0	0	8.350149	-384.831	predict by UNIFAC
MeOH	M2	0	0	-6.60289	-595.595	predict by UNIFAC
MeOH	M3	0	0	-1.32898	-614.16	predict by UNIFAC
M1	water	0	0	-743.429	-240.363	predict by UNIFAC
M1	C2	0	0	-123.047	96.98707	predict by UNIFAC
M1	M2	0	0	51.34585	-56.8088	predict by UNIFAC
M1	C3	0	0	-21.4266	15.00525	predict by UNIFAC
M1	M3	0	0	52.34295	-57.9477	predict by UNIFAC
water	C2	0	0	-131.828	-553.315	predict by UNIFAC
water	M2	0	0	-209.491	-733.907	predict by UNIFAC
water	C3	0	0	-218.847	-606.43	predict by UNIFAC
C2	M2	0	0	34.13477	-37.9913	predict by UNIFAC
C2	C3	0	0	37.46803	-32.4858	predict by UNIFAC
C2	M3	0	0	112.9601	-153.381	predict by UNIFAC
M2	C3	0	0	47.03327	-52.2715	predict by UNIFAC
C3	M3	0	0	65.28362	-85.84	predict by UNIFAC
C1	C3	0	0	-32.0945	30.6595	predict by UNIFAC
MeOH	water	-2.02207	1.88037	753.352	-743.727	from Aspen
MeOH	C1	0.721647	6.37736	-123.13	-2582.67	from Aspen
MeOH	M1	0.536451	-2.40167	-152.96	271.123	from Aspen
MeOH	C3	2.07748	-3.95537	-626.245	843.386	from Aspen
water	M3	-2.0304	-1.06052	-250.646	-186.846	from Aspen
M2	M3	-2.67351	3.69956	1457.7	-1994.35	from Aspen

C1= Oleic acid, C2= Linoleic acid, C3= Palmitic acid, M1= Methyl oleate, M2= Methyl linoleate, M3= Methyl palmitate.

For calculating the saturation vapor pressure of the pure component, the extended Antoine equation was adopted. And constants C_{1i}~C_{9i}, are given in Table S4.

The equation for extend Antoine vapor pressure model is

$$\ln\left(P_i^S\right) = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{C_{7i}} \quad for\ C_{8i} < T < C_{9i}$$

and the unit is $T(K)$ and $P\ (N/Sqm)$

Table S5. Parameters of Extended Antoine Equation [a]

Components	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
CH_3OH	81.768	-6876	0	0	-8.7078	7.19E-06	2	175.47	512.64
H_2O	65.154	-6842.9	0	0.00278 4	-6.13638	3.31E-18	6	319.266	647.3
M1	187.489	-19153	0	0	-22.989	7.28E-06	2	293.049	764
M2	39.907	-15642	0	0	0	0	2	465.149	485.149
M3	-54.972	-6033.7	0	0	12.8029	-1.48E-05	2	335	625
C1	182.069	-20017	0	0	-21.9057	5.92E-06	2	286.528	770
C2	155.131	-18760	0	0	-17.8148	2.61E-06	2	268.148	627
C3	68.923	-11660	0	0	-6.11606	1.66E-06	2	335.66	775
VE	132.38	-20735	0	0	-14.201	7.43E-19	6	276.15	964.3
ST	135.31	-20937	0	0	-14.58	8.11E-19	6	443.15	953.6

[a] **Taken from Aspen Plus V9.0 physical properties databank.**

For calculating the heat of vaporization of the pure component, the model in Aspen Plus is used. And the unit is $H_i^*\ (J/kmol)$ and $T\ (K)$.

(1) The Watson equation is used to calculate heat of vaporization as:

$$\Delta_{vap}H_i^*(T) = \Delta_{vap}H_i^*(T_1)\left(\frac{1 - T/T_{ci}}{1 - T_1/T_{ci}}\right)^{a_i + b(1 - T/T_{ci})} \quad for\ T > T_{min}$$

$\Delta_{vap}H_i^*(T_1)$ Heat of vaporization at temperature T_1

Table S6. The parameters of Watson equation used to calculate heat of vaporization

Components	$\Delta_{vap}H_i^*(T_1)$	T_1	a_i	b	T_{min}

CH_3OH	35277977	337.8	0.371655	0	175.5
H_2O	40683136	373.2	0.310646	0	273.2

(2) The DIPPR equation is used to calculate heat of vaporization

$$\Delta_{vap}H_i^* = C_{1i}(1-T_{ri})^{(C_{2i}+C_{3i}T_{ri}+C_{4i}T_{ri}^2+C_{5i}T_{ri}^3)} \; for \; C_{6i} < T < C_{7i}$$

Where

$$T_{ri} = T/T_{ci}$$

Table S7. The parameters of DIPPR equation used to calculate heat of vaporization

Components	1	2	3	4	5	6	7
M1	1.22E+08	0.395	0	0	0	293.05	764
M3	1.3E+08	1.1283	-1.3017	0.68949	0	303.05	762.2
C1	1.34E+08	0.39553	0	0	0	286.53	781
C2	1.35E+08	0.40785	0	0	0	268.15	775
C3	1.58E+08	0.6023	0	0	0	335.66	785
VE	1.78E+08	0.82989	-0.40978	-0.02118	0	276.15	964.3
ST	1.87E+08	1.0037	-0.67515	0.081215	0	443.15	953.6

(3) The NIST TDE Watson equation is used to calculate heat of vaporization

$$ln\left(\Delta_{vap}H_i^*\right) = C_{1i} + \sum_{m=2}^{nTerms} C_{\mathrm{m}i}\, T_r^{m-2} ln(1-T_r)$$

$$T_r = T/T_c$$

Table S8. The parameters of NIST TDE Watson equation used to calculate heat of vaporization

Components	C_{1i}	C_{2i}	C_{3i}	C_{4i}	T_{ci}	$nTerms$	T_{lower}	T_{upper}
M2	19.16569	1.90251	-1.46074	0.128814	773	4	233.9	773

In addition, we list some physical property parameters used in the calculated in Aspen Plus.

Table S9. Pure component physical properties parameters

Parameters	DHVLB	GMUQQ	GMUQR	MUP	MW	PC	TB	TC	VB	VC	ZC
Units	cal/mol			debye		kPa	K	K	cc/mol	cc/mol	
CH3OH	8426	1.432	1.4311	1.7	32.04216	8095.868	337.8	512.6	43.49642	117.9161	0.224
H2O	9717	1.4	0.92	1.8	18.01528	22048.32	373.2	647.3	19.63607	55.89534	0.229

M1		11	13.3619	1.588902	296.4936	1280	617	764		1059.99	0.214
M2		10.784	13.10086		294.4778	1215.06	551.32	773		1210.773	0.228901
M3		10.136	12.2479	1.588902	270.4558	1650	599.299	763		1150	0.224
C1		10.496	12.7456	1.439007	282.4668	1390	632	770		1000	0.214
C2		9.432	12.5135	1.217161	280.4509	1300	627	775		990	0.217
C3		9.632	11.6289	1.738801	256.4289	1500	624.15	775		916.998	0.212
VE	18771.21	13.896	19.3408	2.27543	430.7148	1080	787.8	964.3	698.722	1720	0.232
ST	18990.37	12.204	18.2334	1.930665	412.6995	1138	778	953.6	546.024	1440	0.207

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Parameters	description
DHVLB	enthalpy of vaporation at TB
GMUQQ	molecular area parameter for UNIQUAC activity coefficient model
GMUQR	molecular volume parameter for UNIQUAC activity coefficient model
MUP	dipole moment
MW	molecular weight
PC	critical pressure
TB	normal boiling point
TC	critical temperature
VB	liquid mole volume at TB
VC	critical volume
ZC	critical compressibility factor

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Section 4. The input specifications used in base-case Aspen Plus simulations.

Table S10 Quality composition of SODD feed stream in simulation process.

Component	Concentration wt %
Tocopherol	25
Sitosterol	25
Oleic Acid (C18:1)	25
Linoleic acid (C18:2)	5
Palmitic acid (C16:0)	20

Table S11. The input specifications used in base-case Aspen Plus simulations.

Parameter	specification
Property method	UNIFAC-DMD
Interaction parameter value	UNIFAC (Table S3.)
Reaction kinetics	Table 5.
RADFRAC	
No. of stages	9
Rectifying stages	2
Reactive stages	3
Striping stages	2

Resident time per stage	120s
Valid phase	Vapor-liquid-liquid
Feed temperature and pressure	60℃ and 1atm

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Section 5. Equation of TAC and equipment sizing.

Table S12. Basis of economics estimation

Column vessel	column diameter(D) = Aspen tray sizing
	column length(L) = NT trays with 2 ft spacing plus 20% extra length
	investment cost = 17640D1.066L0.802 where D and L are in m
Reboilers	heat transfer coefficient = 0.568kW/ (K m2)
	differential temperature = stream temperature – column base temperature
	investment cost=7286A0.65 where A is in m2
Condensers	heat transfer coefficient =0.852Kw/ (K m2)
	differential temperature=log-mean temperature difference of inlet and outlet temperature differences
	investment cost =7296A0.65 where A is in m2
Utility prices	low pressure steam (160℃) = $ 7.78/GJ
	medium pressure steam (184℃) = $ 8.22/GJ
	high pressure steam (254℃) = $ 9.88/GJ
	cooling water = $ 0.354/GJ
TAC = (investment cost/payback period) + operating cost	payback period = 3years