MODELLING OF BIODIESEL SYNTHESIS WITH AND WITHOUT GLYCEROL REMOVAL FROM REACTION MIXTURE

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A deterministic mathematical model was developed to describe the transesterification of a vegetable oil with methanol in a perfectly stirred reactor, in the presence of a homogeneous base catalyst. Depending on the operation mode (batch, batch followed by semi-continuous process with glycerol flow, fed-batch followed by continuous process with feed mixture flow and glycerol flow, fed-batch with methanol feed, and fed-batch with oil feed) and methanol/oil molar ratio (R=2, 4, 6, 8), the reaction equilibrium can be shifted and the biodiesel yield enhanced. Simulated dynamics of mass fractions of reactants and reaction products for different operation modes and values of R were presented. Except for fed-batch reactor with oil feed, biodiesel yields larger than 90% were obtained for R≥4. Transesterification efficiency can be improved by removing the glycerol from the system, after its separation at the bottom of the reactor.

Keywords: biodiesel, modelling, perfectly stirred reactor, transesterification

1. Introduction

In the current context of fossil fuel depletion, environmental degradation, and energy security, researchers and producers are heavily focusing on alternative energy sources [1-3]. Biomass is a renewable energy source that is increasingly used to obtain biofuels, thermal and electrical energy [4,5]. Biofuels can be produced from biomass by various techniques, *e.g.*, biodiesel by transesterification, bioalcohols (bioethanol, biobuthanol) by alcoholic fermentation, biogas by anaerobic (co-)digestion, bio-oil, bio-char, and biogas by pyrolysis or hydrothermal liquefaction [4-8].

Biodiesel is a renewable and biodegradable fuel with near-zero content of sulfur and aromatics [9-11]. The term biodiesel refers to fatty acid mono-alkyl

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esters obtained by transesterification of triglycerides from vegetable oils or animal fats with a short chain alcohol (*e.g.*, methanol, ethanol). Transesterification generally occurs in the presence of homogeneous/heterogeneous catalyst (base, acid) or biocatalyst (free/immobilized enzyme) [1-3,11-13]. Biodiesel synthesis is commonly performed in batch, fed-batch, and continuous stirred reactors [14]. Batch operating mode is widely used in small and medium scale biodiesel production units [15].

At present, most of the biodiesel is produced in batch reactors using vegetable oils and methanol as reactants and NaOH or KOH as homogeneous base catalyst. Reversibile transesterification reactions (1)-(3) occur as follows: a triglyceride (*TG*) reacts with methanol (*ME*) resulting in fatty acid methyl ester (FAME) (*E*) and a diglyceride (*DG*), *DG* continues transesterification to *E* and corresponding monoglyceride (*MG*), *MG* reacts with *ME* producing *E* and glycerol (*G*) [9,15-18].

$$TG + ME \underset{k_2}{\overset{k_1}{\Longleftrightarrow}} DG + E \tag{1}$$

$$DG + ME \underset{k_4}{\overset{k_3}{\Longleftrightarrow}} MG + E \tag{2}$$

$$MG + ME \underset{k_6}{\overset{k_5}{\Longleftrightarrow}} G + E \tag{3}$$

Transesterifications of glycerides with methanol, which are equilibrium reactions, can be controlled by removing a reaction product. The glycerol can be easily removed during the process because it is insoluble in the reaction mixture and has a higher density than FAME. Glycerol separation during the process can lead to an increase in the transesterification process efficiency [19].

Modelling is an effective tool to predict and improve the performances of processes with/without (bio)chemical reaction [20-22]. A mathematical model based on total and partial mass balance equations was developed to describe the transesterification of a vegetable oil with methanol in a perfectly stirred reactor, in the presence of a homogeneous base catalyst. Simulated dynamics of mass fractions of reactants and reaction products for 5 operating modes (*batch*, *batch followed by semi-continuous process with glycerol flow*, *fed-batch followed by continuous process with feed mixture flow and glycerol flow*, *fed-batch with methanol feed*, and *fed-batch with oil feed*) and different levels of methanol/oil molar ratio (2÷8) were presented.

2. Modelling of transesterification process in a perfectly stirred reactor

2.1. Kinetics of vegetable oil transesterification using homogeneous base catalyst

Kinetics of transesterification of triglycerides from vegetable oils with methanol, under different operation conditions (usually homogeneous base catalyst, methanol/oil molar ratio of 6/1, temperature of 60 °C, and catalyst concentration of 1% w/w), have been extensively studied [9,15-18].

Reaction rates of reversible reactions (1)-(3), v_{rk} (k=1..3) [kmol/(m^3·s)], are expressed by Eqs. (4)-(6), where k_i (i=1...6) [m^3/(kmol·s)] is rate constant and c_j (kmol/m^3) the molar concentration of species j (*ME*, *TG*, *DG*, *MG*, *G*, *E*) [9,15].

$$v_{r1} = k_1 c_{TG} c_{ME} - k_2 c_{DG} c_E \tag{4}$$

$$v_{r2} = k_2 c_{DG} c_{ME} - k_4 c_{MG} c_E \tag{5}$$

$$v_{r3} = k_5 c_{MG} c_{ME} - k_6 c_G c_E \tag{6}$$

The dependence of reaction rate constant (k_i) on absolute temperature (T) is expressed by Arrhenius equation (7), where k_{i0} [m^3/(kmol·s)] is the pre-exponential factor, E_i (J/kmol) the activation energy, and R [8314 J/(kmol·K)] the universal gas constant.

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right),\ i=1..6 \tag{7}$$

2.2. Physical model

A simplified diagram of an installation containing a perfectly stirred reactor is shown in Fig. 1. Five operation modes were taken into account, *i.e.*:

(i) *batch* − the valves V_1, V_2, V_5, and V_6 are opened, the reactor is quickly fed (with a flow rate F) with the feed mixture until a pre-determined level of reaction mixture volume (V_R) is attained, then the valves are closed; finally the stirring is stopped and a decantation process takes place; V_3 valve is opened and the reaction mixture leaves the reactor, first glycerol (separated at the bottom of reactor), then biodiesel;

(ii) *batch followed by semi-continuous process with glycerol flow* − the valves V_1, V_2, V_5, and V_6 are opened, the reactor is quickly fed until the level V_R is attained, then the valves are closed; a batch transesterification process occurs for a time (τ_{batch}) necessary for the formation and separation of

glycerol at the bottom of reactor, then the valve V_4 is opened and the glycerol leaves the system with a flow rate F_e;

(iii) *fed-batch followed by continuous process with feed mixture flow and glycerol flow* − the valves V_1, V_2, V_5, and V_6 are opened, the reactor is fed with a flow rate F until the level V_R is attained, then the valve V_4 is opened and the glycerol leaves the system with a flow rate $F_e=F$;

(iv) *fed-batch with methanol feed* − the valves V_1, V_2, and V_6 are opened and the reactor is quickly fed with a calculated oil volume; then the valve V_6 is closed, the valve V_5 is opened, and the methanol is fed throughout the process duration;

(v) *fed-batch with oil feed* − the valves V_1, V_2, and V_5 are opened and the reactor is quickly fed with a calculated methanol volume; then the valve V_5 is closed, the valve V_6 is opened, and the oil is fed throughout the process duration.

Depending on the operation mode, *i.e.*, *batch*, *batch followed by semi-continuous process*, *fed-batch followed by continuous process*, *semi-continuous process* (*fed-batch with either methanol or oil feed*), the reaction equilibrium can be shifted and the biodiesel yield enhanced.

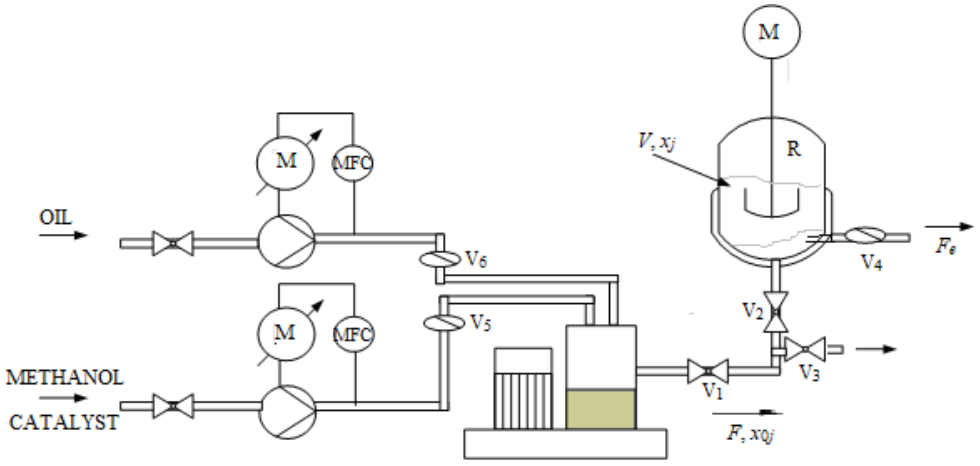

Fig. 1. Simplified diagram of an installation with a perfectly stirred reactor: F − mass flow rate of feed mixture (oil + methanol + catalyst); F_e − mass flow rate of G; V − volume of reaction mixture in the reactor; x_{0j} − mass fraction of species j (*ME*, *TG*, *DG*, *MG*, *G*, and *E*) in the feed mixture; x_j − mass fraction of species j in the reaction mixture; M − motor; MFC − mass flow controller; R − reactor; V_1..V_6 − valves.

2.3. Mathematical model

Mathematical model describing the biodiesel synthesis process consists of total and partial (species *j=ME, TG, DG, MG, G, E*) material balance equations (8)-(10), where F (kg/s) is the mass flow rate of feed mixture (consisting of oil, methanol, and NaOH or KOH homogeneous base catalyst), F_e (kg/s) the mass flow rate of *G*, V (m^3) the volume of reaction mixture, x_{0j} (kg/kg) the mass fraction of species j in the feed mixture, x_j (kg/kg) the mass fraction of species j in the reaction mixture, ϕ_j (kg/s) the participation of species j in the reactions (1)-(3), ρ_m (kg/m^3) the density of reaction mixture, and τ (s) the time. The parameters ϕ_j and ρ_m were determined using Eqs. (11)-(17), where M_j (kg/kmol) is the molar mass of species j, v_{rk} [$kmol/(m^3 \cdot s)$] the reaction rate of transesterification reaction k (k=1..3), and ρ_j (kg/m^3) the density of species j.

$$\frac{\mathrm{d}V}{\mathrm{d}\tau} = \frac{F}{\rho_m} - \frac{F_e}{\rho_m} \tag{8}$$

$$\frac{\mathrm{d}x_j}{\mathrm{d}\tau} = \frac{F}{\rho_m V}(x_{oj} - x_j) + \frac{\phi_j}{\rho_m V},\ j=ME, TG, DG, MG, E \tag{9}$$

$$\frac{\mathrm{d}x_j}{\mathrm{d}\tau} = \frac{F}{\rho_m V}(x_{oj} - x_j) + \frac{\phi_j}{\rho_m V} - \frac{F_e}{\rho_m V}x_j,\ j=G \tag{10}$$

$$\phi_1 = -(v_{r1} + v_{r2} + v_{r3})VM_{ME} \tag{11}$$

$$\phi_2 = -v_{r1}VM_{TG} \tag{12}$$

$$\phi_3 = (v_{r1} - v_{r2})VM_{DG} \tag{13}$$

$$\phi_4 = (v_{r2} - v_{r3})VM_{MG} \tag{14}$$

$$\phi_5 = v_{r3}VM_G \tag{15}$$

$$\phi_6 = (v_{r1} + v_{r2} + v_{r3})VM_E \tag{16}$$

$$\frac{1}{\rho_m} = \sum_j \frac{x_j}{\rho_j} \tag{17}$$

3. Results and discussions

Simulated dynamics of mass fractions of species *j* (*ME, TG, DG, MG, G,* and *E*) for 5 operating modes (*batch, batch followed by semi-continuous process with glycerol flow, semi-continuous* (*fed-batch*) *followed by continuous process with feed mixture flow and glycerol flow, fed-batch with methanol feed*, and *fed-*

batch with oil feed) at different levels of methanol/oil molar ratio (2, 4, 6, and 8) are presented.

The following issues were taken into account to simulate the process based on Eqs. (4)-(17): (i) V_R=20 m^3; (ii) τ_{batch}=5 min for *batch followed by semi-continuous process with glycerol flow*; (iii) excepting *fed-batch followed by continuous process with feed mixture flow and glycerol flow*, the reaction time was of 80 min; (iv) isothermal process (60 ºC); (v) reaction rate constants k_i (i=1..6) at 60 ºC were determined using Eq. (7), based on values of kinetic parameters E_i and k_{i0} reported in the literature [2,9,15-18].

3.1. Batch process

Characteristic data of *batch process, i.e.*, mass fractions of species j (*ME*, *TG*, *DG*, *MG*, *G*, and *E*) in the feed mixture (x_{0j}), initial mass fractions of species j in the reactor (x_{j0}), feed mass flow rate (F), glycerol mass flow rate (F_e), and biodiesel yield (Y), at different values of methanol/oil molar ratio (R=2÷8) are given in Table 1. Dynamics of mass fractions of species j in the reactor, $x_j(\tau)$, for R=2÷8, which are shown in Fig. 2, indicate the following issues: (i) values of mass fractions of FAME (x_E=0÷0.75) for $R\geq$6 are similar during the transesterification process (τ=0÷80 min); (ii) values of mass fractions of methanol (x_{ME}), triglyceride (x_{TG}), and glycerol (x_G) are almost constant for $\tau\geq$20 min at any value of R; (iii) values x_{TG} (0.03÷0.93) and x_G (0÷0.08) for $R\geq$4 are similar during the process.

Table 1

Characteristic data of *batch process* (*j=ME, TG, DG, MG, G, E*)

No.	R	x_{0j}	x_{ME0}	x_{TG0}	x_{DG0}	x_{MG0}	x_{G0}	x_{E0}	F	F_e	Y
	(mol/mol)	(kg/kg)							(kg/min)		(%)
1	2	0	0.07	0.93	0	0	0	0	0	0	71.6
2	4	0	0.13	0.87	0	0	0	0	0	0	91.4
3	6	0	0.18	0.82	0	0	0	0	0	0	96.0
4	8	0	0.23	0.77	0	0	0	0	0	0	98.6

3.2. Batch followed by semi-continuous process with glycerol flow

Characteristic data of *batch followed by semi-continuous process with glycerol flow, i.e.*, x_{0j}, x_{j0}, F, F_e, and Y, where *j=ME, TG, DG, MG, G, E*, at different values of methanol/oil molar ratio (R=2÷8) are given in Table 2. Comparing these tabulated data with those presented in Table 1 (for *batch process*), slightly higher values (up to 1%) of biodiesel yield (Y) were obtained for $R\geq$4 in *batch followed by semi-continuous process with glycerol flow*. Dynamics of mass fractions of species j in the reactor, $x_j(\tau)$, for R=2÷8, which are shown in Fig. 3, indicate the following issues: (i) values of mass fractions of FAME (x_E=0÷0.74) for $R\geq$6 are similar during the transesterification process (τ=0÷80 min); (ii) values of mass fractions of methanol (x_{ME}) and triglycerides (x_{TG}) are

almost constant for $\tau \geq 20$ min at any value of R; (iii) values x_{TG} (0.03÷0.93) and x_G (0÷0.06) for $R \geq 4$ are similar during the process; (iv) $x_G \leq 0.005$ for $\tau = 80$ min at any value of R.

Table 2

Characteristic data of *batch followed by semi-continuous process with glycerol flow* (*j=ME, TG, DG, MG, G, E*)

No.	R	x_{0j}	x_{ME0}	x_{TG0}	x_{DG0}	x_{MG0}	x_{G0}	x_{E0}	F	F_e		Y
	(mol/mol)	(kg/kg)							(kg/min)	(kg/min)		(%)
										$\tau \leq 5$ min	$\tau > 5$ min	
1	2	0	0.07	0.93	0	0	0	0	0	0	19	71.6
2	4	0	0.13	0.87	0	0	0	0	0	0	19	92.1
3	6	0	0.18	0.82	0	0	0	0	0	0	19	97.0
4	8	0	0.23	0.77	0	0	0	0	0	0	19	99.3

3.3. Fed-batch followed by continuous process with feed mixture flow and glycerol flow

This operation mode consists in 2 consecutive stages: (i) *fed-batch* operation until the volume of reaction mixture in the reactor attains a pre-established level ($\tau \leq 80$ min) and (ii) *continuous* operation characterized by $F=F_e$ ($80 < \tau \leq 160$ min). Characteristic data of *fed-batch followed by continuous process*, *i.e.*, x_{0j}, x_{j0}, F, F_e, and Y, where $j=ME$, TG, at different values of methanol/oil molar ratio ($R=2 \div 8$) are given in Table 3. The values $x_{0j}=x_{j0}=0$ for $j=DG$, MG, G, E were not included in Table 3. Comparing these tabulated data with those presented in Tables 1 and 2 (for *batch* and *batch followed by semi-continuous process with glycerol flow*), the following issues are noticed: (i) values of biodiesel yield (Y) up to 13% higher were obtained for $R=2$ and (ii) values of Y up to 4% lower were obtained for $R \geq 4$ in *fed-batch followed by continuous process with feed mixture flow and glycerol flow.*

Table 3

Characteristic data of *fed-batch followed by continuous process*

No.	R	x_{0ME}	x_{0TG}	x_{ME0}	x_{TG0}	F	F_e		Y
	(mol/mol)	(kg/kg)				(kg/min)	(kg/min)		(%)
							$\tau \leq 80$ min	$\tau > 80$ min	
1	2	0.07	0.93	0.01	0.99	250	0	250	80.6
2	4	0.13	0.87	0.01	0.99	250	0	250	90.2
3	6	0.18	0.82	0.01	0.99	250	0	250	93.4
4	8	0.23	0.77	0.01	0.99	250	0	250	95.3

Dynamics of mass fractions of species j in the reactor, $x_j(\tau)$, for $R=2 \div 8$, which are shown in Fig. 4, indicate that: (i) values of mass fractions of FAME ($x_E=0 \div 0.6$), triglyceride ($x_{TG}=0.10 \div 0.99$), and glycerol ($x_G=0 \div 0.1$) for $R \geq 4$ are similar during the transesterification process ($\tau=0 \div 160$ min); (ii) values of mass

fractions of methanol (x_{ME}), triglyceride (x_{TG}), and diglyceride (x_{DG}) are almost constant for $\tau \geq 80$ min at any value of R.

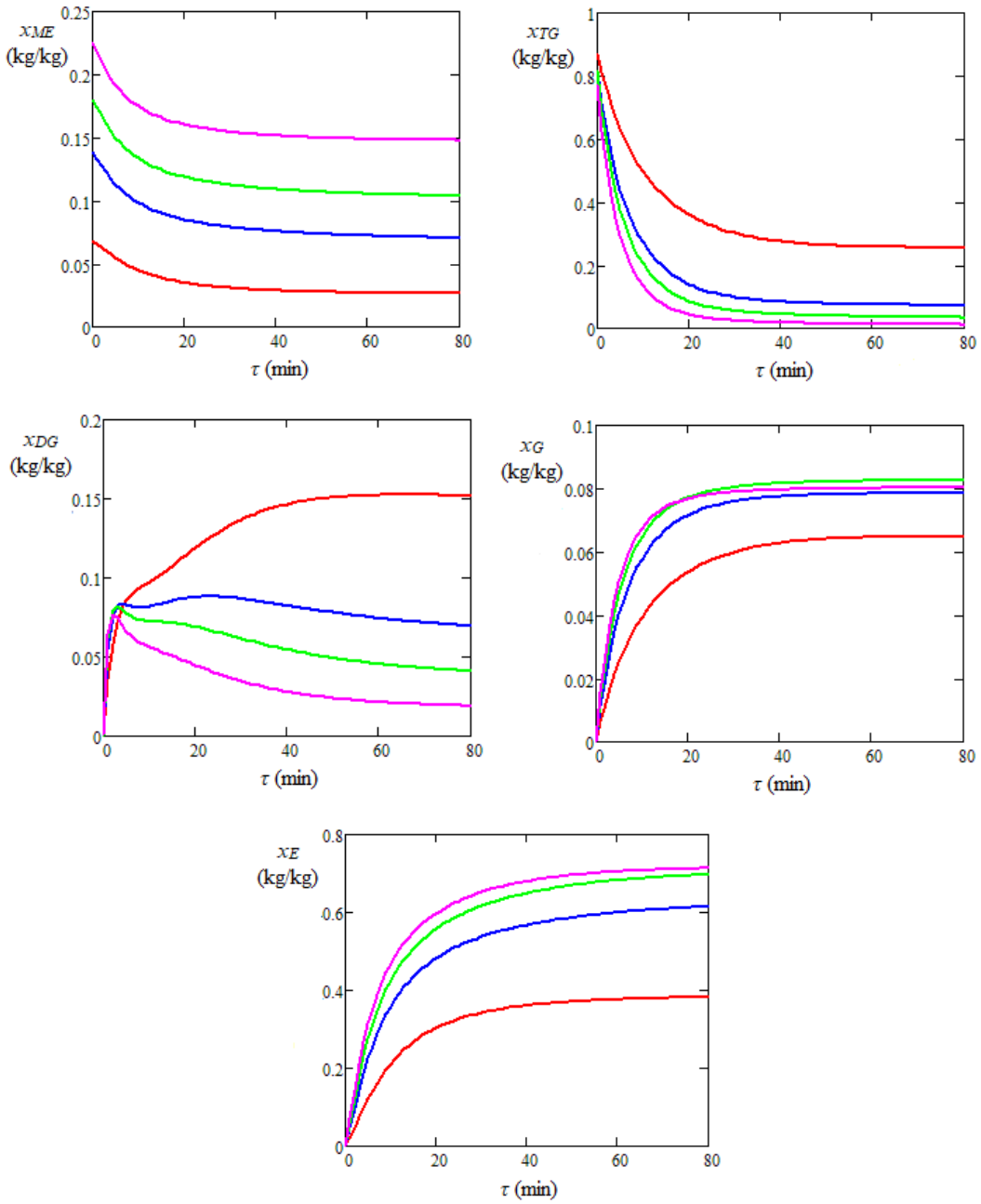

Fig. 2. Dynamics of mass fractions of species *j* [methanol (ME), triglyceride (TG), diglyceride (DG), glycerol (G), and FAME (E)] for *batch process* at different levels of methanol/oil molar ratio: 2 (red), 4 (blue), 6 (green), and 8 (pink).

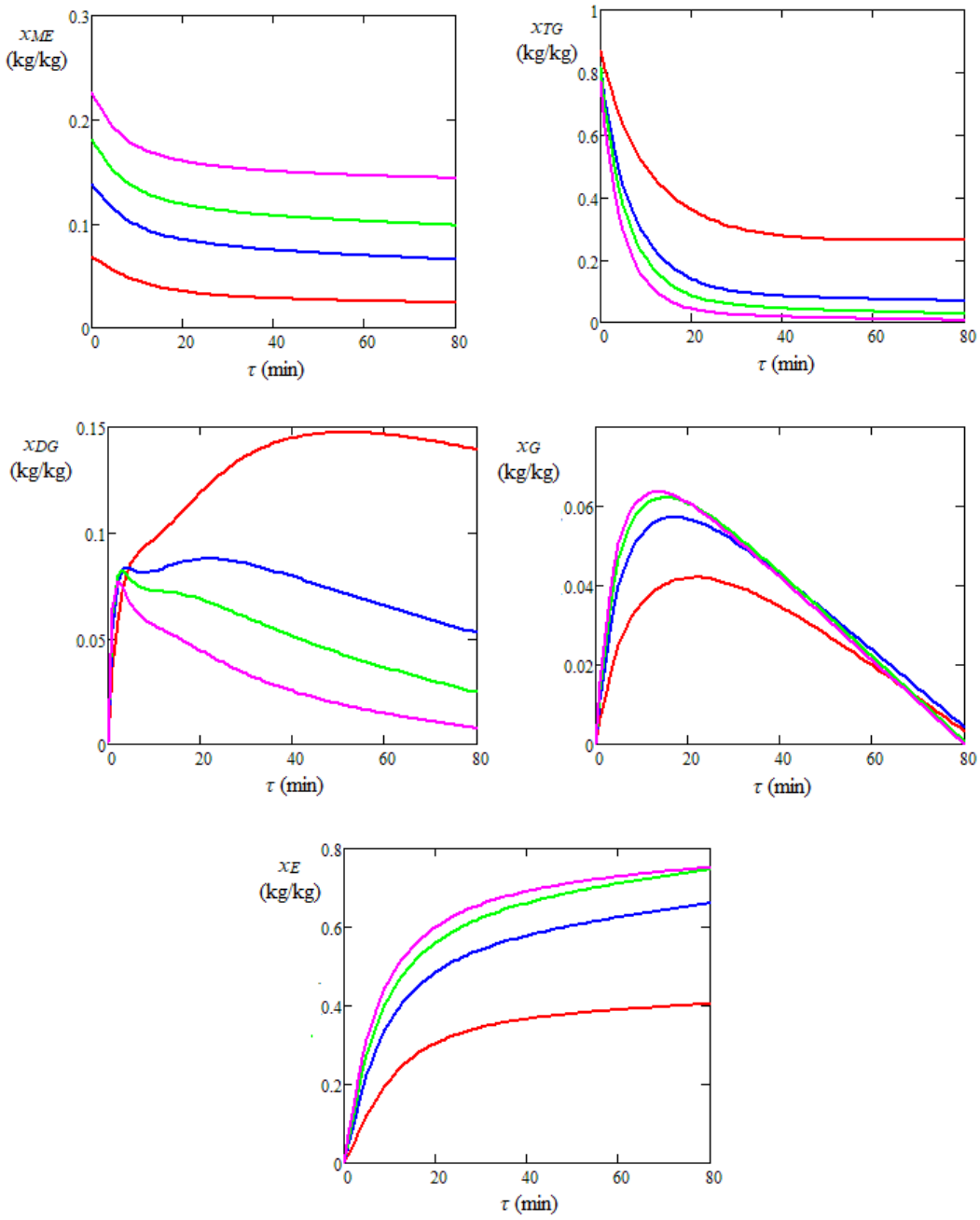

Fig. 3. Dynamics of mass fractions of species *j* [methanol (ME), triglyceride (TG), diglyceride (DG), glycerol (G), and FAME (E)] for *batch followed by semi-continuous process with glycerol flow* at different levels of methanol/oil molar ratio: 2 (red), 4 (blue), 6 (green), and 8 (pink).

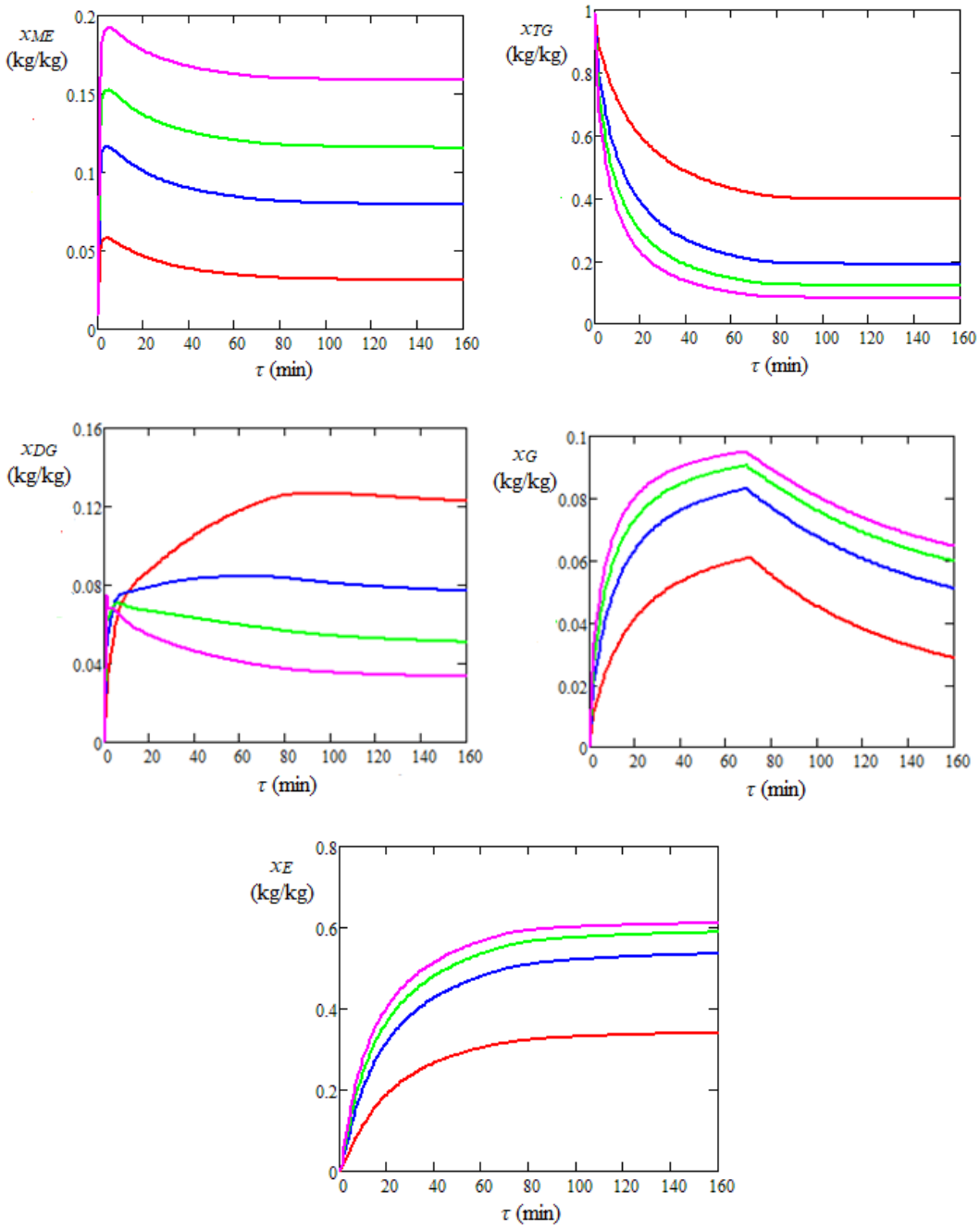

Fig. 4. Dynamics of mass fractions of species *j* [methanol (ME), triglyceride (TG), diglyceride (DG), glycerol (G), and FAME (E)] for *fed-batch followed by continuous process with feed mixture flow and glycerol flow* at different levels of methanol/oil molar ratio: 2 (red), 4 (blue), 6 (green), and 8 (pink).

3.4. Fed-batch process with methanol feed

Heated oil is first fed into the reactor and then the methanol is fed over the oil. Characteristic data of *fed-batch process with methanol feed, i.e.*, x_{0j}, x_{j0}, F, F_e, and Y, where j=*ME*, *TG*, *DG*, *MG*, *G*, *E*, at different values of methanol/oil molar ratio (R=2÷8) are given in Table 4. Values of biodiesel yield (72.5÷98.5%) are almost similar with those obtained for *batch process* (71.6÷98.6%) and *batch followed by semi-continuous process with glycerol flow* (71.6÷99.3%).

Dynamics of mass fractions of species j in the reactor, $x_j(\tau)$, for R=2÷8, which are shown in Fig. 5, indicate similar values of mass fractions of FAME (x_E=0÷0.68), glycerol (x_G=0÷0.10), and triglyceride (x_{TG}=0.04÷1) for $R\geq$6 during the transesterification process (τ=0÷80 min).

Table 4

Characteristic data of *fed-batch process with methanol feed*

No.	R	x_{0ME}	x_{0E}	x_{ME0}	x_{TG0}	x_{DG0}	x_{MG0}	x_{E0}	F	F_e	Y
	(mol/mol)	(kg/kg)							(kg/min)		(%)
1	2	0.998	0.002	0.010	0.980	0.002	0.003	0.005	17	0	72.5
2	4	0.998	0.002	0.010	0.980	0.002	0.003	0.005	34	0	91.2
3	6	0.998	0.002	0.010	0.980	0.002	0.003	0.005	45	0	96.2
4	8	0.998	0.002	0.010	0.980	0.002	0.003	0.005	56	0	98.5

3.5. Fed-batch process with oil feed

The methanol is first fed into the reactor and then the heated oil is fed over the methanol. Characteristic data of *fed-batch process with oil feed, i.e.*, x_{0j}, x_{j0}, F, F_e, and Y, where j=*ME*, *TG*, *DG*, *MG*, *G*, *E*, at different values of methanol/oil molar ratio (R=2÷8) are given in Table 5. Values of biodiesel yield (65.8÷90.9%) are lower than those obtained for the other 4 operation modes, *i.e.*, *batch* (71.6÷98.6%), *batch followed semi-continuous process with glycerol flow* (71.6÷99.3%), *fed-batch followed by continuous process* (80.6÷95.3%), and *fed-batch with methanol feed* (72.5÷98.5%). Dynamics of mass fractions of species j in the reactor, $x_j(\tau)$, for R=2÷8, which are shown in Fig. 6, indicate similar values of mass fractions of FAME (x_E=0÷0.60) for $R\geq$6 during the transesterification process (τ=0÷80 min).

Table 5

Characteristic data of *fed-batch process with oil feed*

No.	R	x_{0TG}	x_{0DG}	x_{0MG}	x_{ME0}	x_{DG0}	x_{MG0}	x_{E0}	F	F_e	Y
	(mol/mol)	(kg/kg)							(kg/min)		(%)
1	2	0.990	0.005	0.005	0.992	0.001	0.002	0.005	210	0	65.8
2	4	0.990	0.005	0.005	0.992	0.001	0.002	0.005	196	0	78.9
3	6	0.990	0.005	0.005	0.992	0.001	0.002	0.005	184	0	86.9
4	8	0.990	0.005	0.005	0.992	0.001	0.002	0.005	175	0	90.9

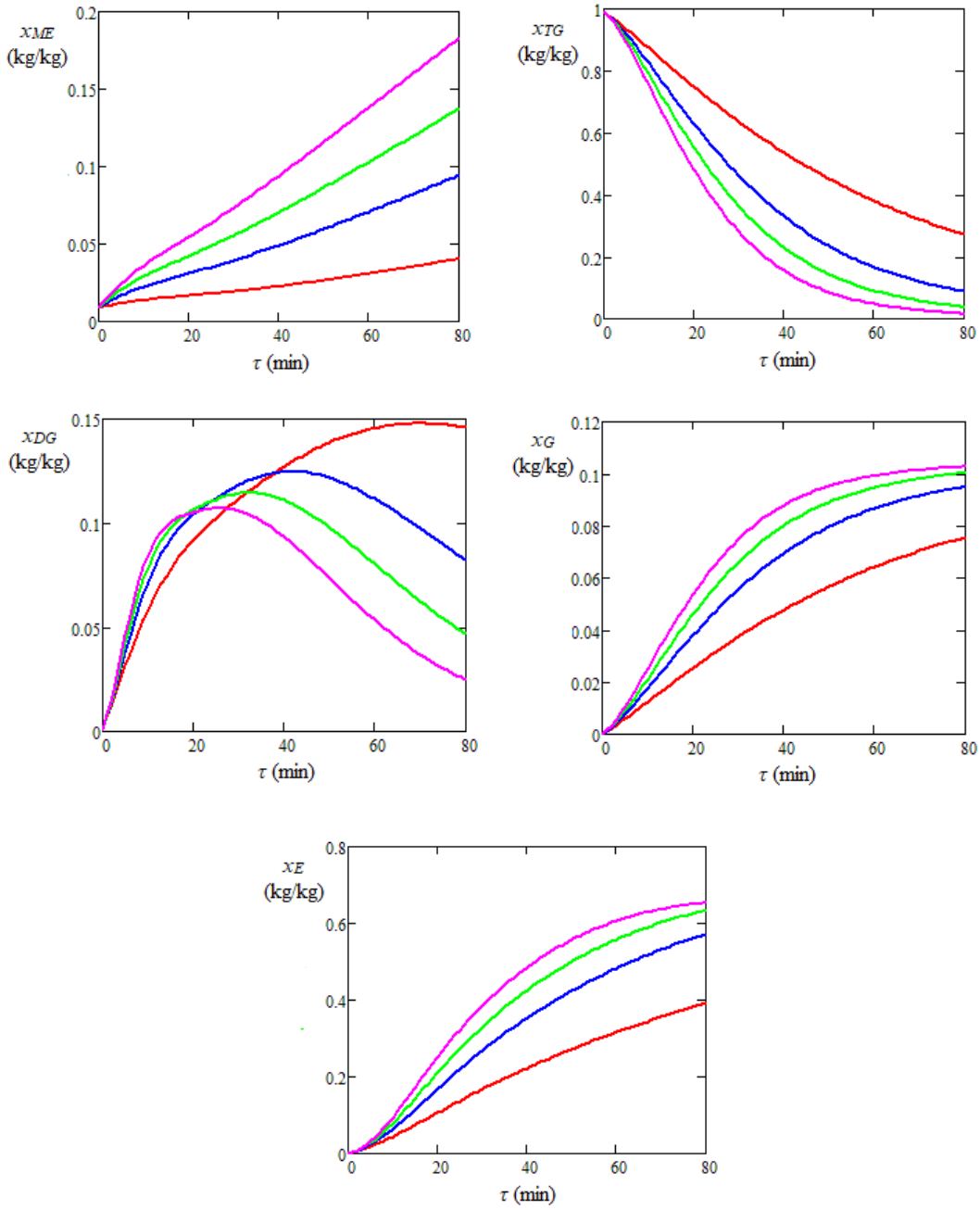

Fig. 5. Dynamics of mass fractions of species *j* [methanol (ME), triglyceride (TG), diglyceride (DG), glycerol (G), and FAME (E)] for *fed-batch process with methanol feed* at different levels of methanol/oil molar ratio: 2 (red), 4 (blue), 6 (green), and 8 (pink).

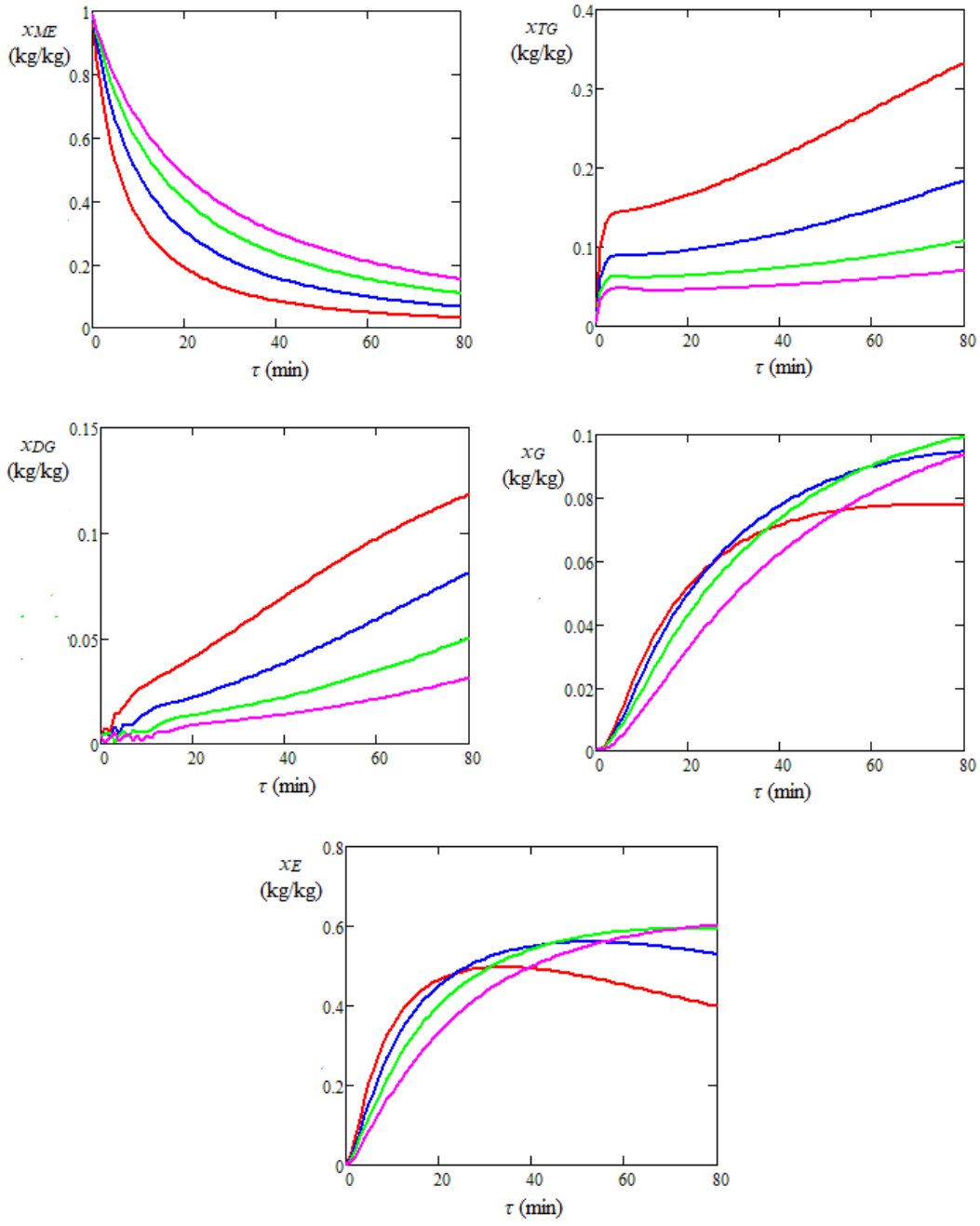

Fig. 6. Dynamics of mass fractions of species *j* [methanol (ME), triglyceride (TG), diglyceride (DG), glycerol (G), and FAME (E)] for *fed-batch process with oil feed* at different levels of methanol/oil molar ratio: 2 (red), 4 (blue), 6 (green), and 8 (pink).

6. Conclusions

Process performances for transesterification of a vegetable oil with methanol in a perfectly stirred reactor, in the presence of a homogeneous base catalyst, were predicted using a mathematical model based on total and partial mass balance equations. Simulated dynamics of mass fractions of reactants and reaction products for 5 operating modes, *i.e.*, *batch* (*B*), *batch followed by semi-continuous process with glycerol flow* (*BS*), *fed-batch followed by continuous process with feed mixture flow and glycerol flow* (*FBC*), *fed-batch with methanol feed* (*FBM*), and *fed-batch with oil feed* (*FBO*), at different levels of methanol/oil molar ratio (R=2, 4, 6, 8) were presented.

Depending on the operation mode and methanol/oil ratio, the reaction equilibrium can be shifted and the biodiesel yield enhanced. Except for *FBO* operation mode, biodiesel yields (Y) larger than 90% were obtained for $R \geq 4$, *i.e.*, Y_B=91.4÷98.6%, Y_{BS}=92.1÷99.3%, Y_{FBC}=90.2÷95.3%, and Y_{FBM}=91.2÷98.5%. Transesterification efficiency can be increased by removing the glycerol from the reaction mixture, after its separation at the bottom of the reactor.

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