Biodiesel production using liquid – liquid film reactors

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Research questions

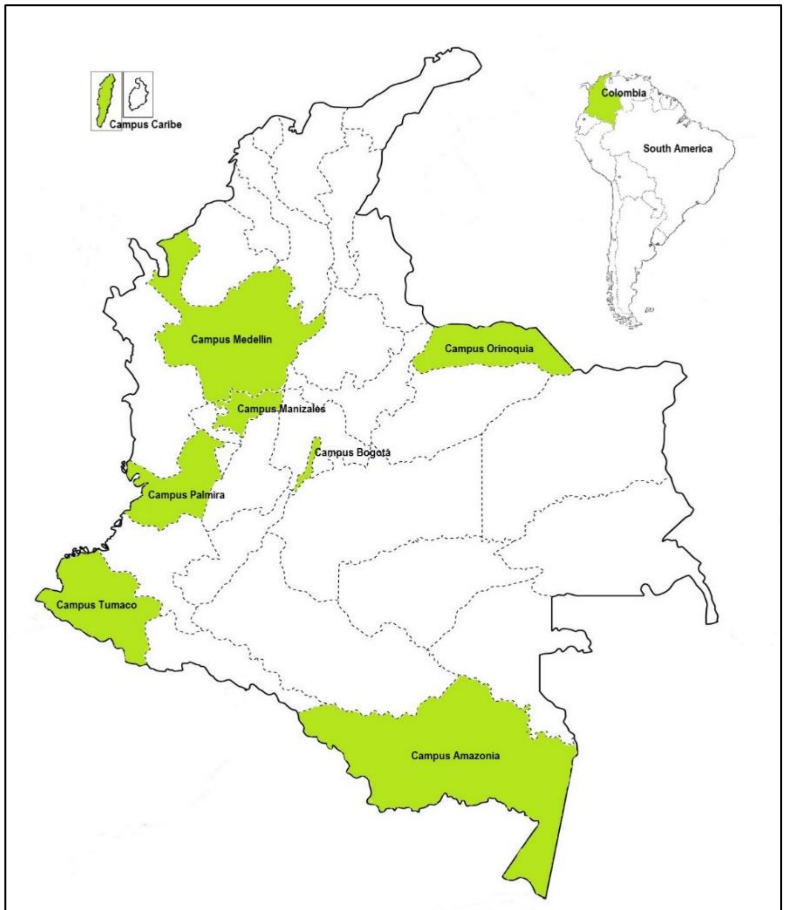
Is it possible to produde biodiesel using liquid – liquid film reactors?

If it is possible, is the productivity higher than the obtained in typical industrial process, where CSTR are used implementing three or more reaction-separation stages?

Outline

- Universidad Nacional de Colombia
- Biodiesel production in Colombia
- Falling Film Contactors
- Co-current operation
- Counter-current operation
- Co-current integrated with hollow fiber membrane (HFM)
- Conclusion

Universidad Nacional de Colombia



8	Campus
52,550	Students
94	Undergraduate programs
361	Graduate programs

School of Engineering

- Civil and Agriculture
- Chemical and Environmental
- Electric and Electronics
- Mechanical and Mechatronics
- Systems and Industrial

263 Professors

6269 Undergraduate students

651 Graduate students

Palm oil production in Colombia

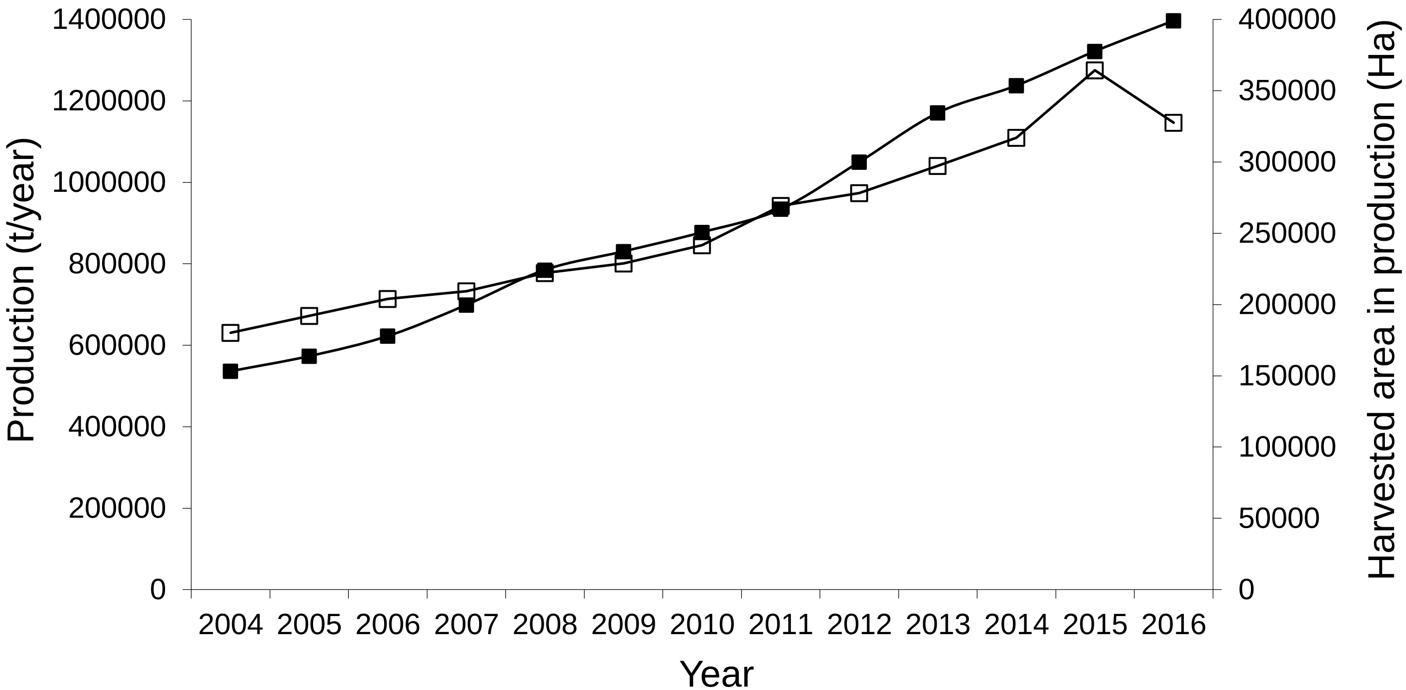


Figure 1. Oil palm harvested area in production (▫) and palm oil production (▪)

Data from http://www.fedebiocombustibles.com/nota-web-id-488.htm, retrieved July 2018

Biodiesel production

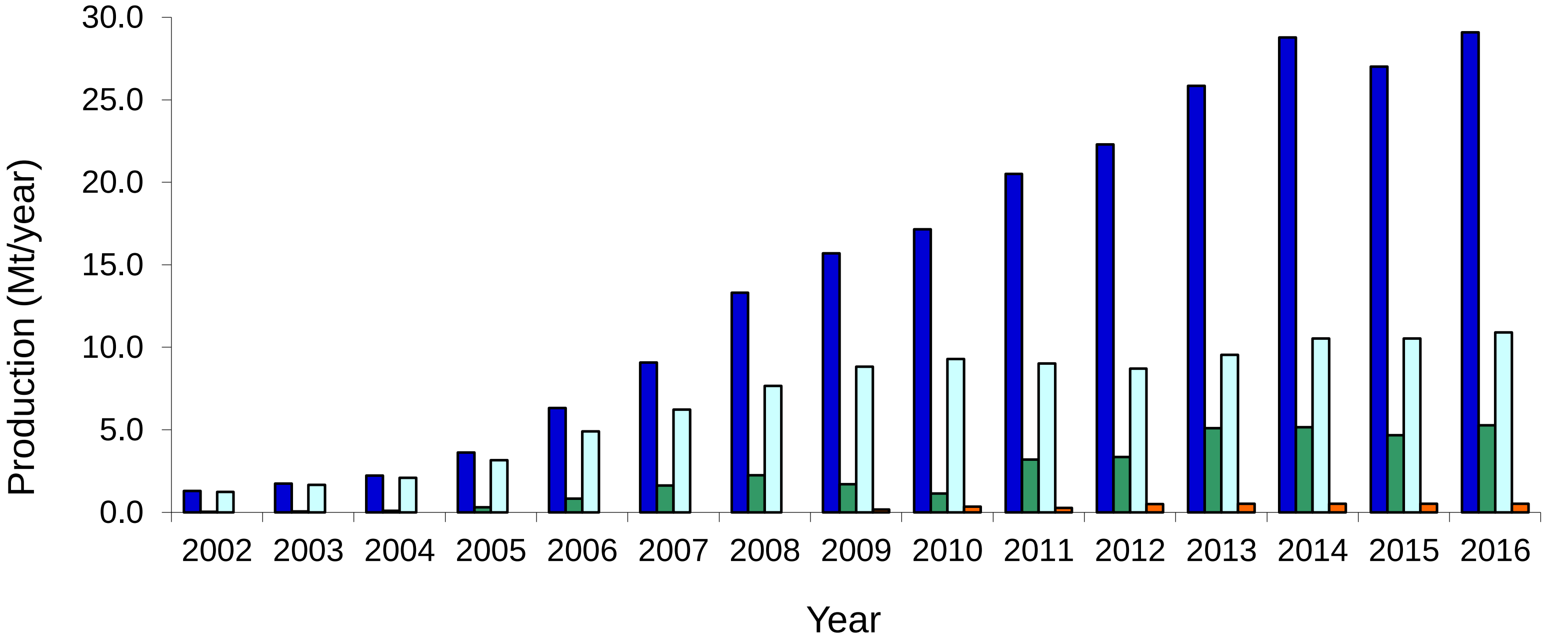


Figure 2. Biodiesel production (▪) World (▪) United States (▪) European Union (▪) Colombia
Data from http://www.eia.gov/cfapps/ipdbproject, retrieved July 2017

Biodiesel production in Colombia

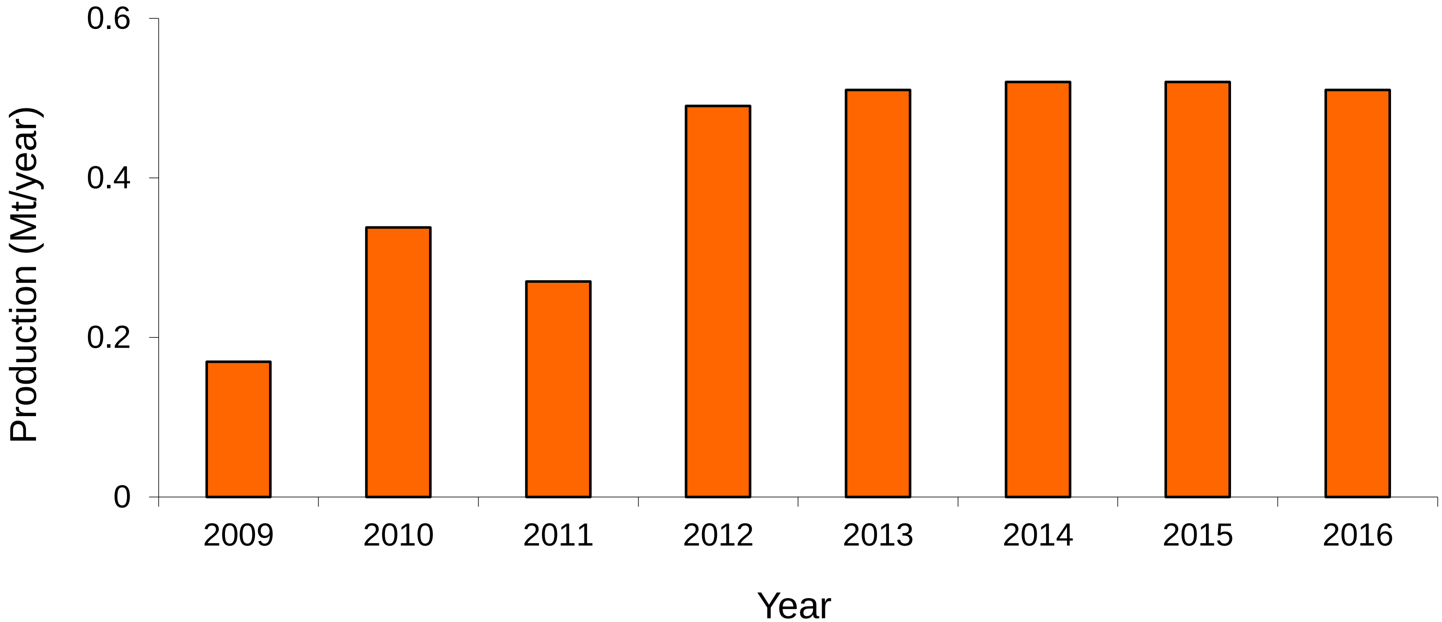


Figure 3. Biodiesel production in Colombia (0.5 Mt/year)
Data from http://www.fedebiocombustibles.com/nota-web-id-488.htm, retrieved July 2018

Why did we propose the use LLFC in biodiesel production?

- To promote the contact of two phases (ester and alcohol – rich) without dispersing one phase into the other.

- To reduce separation time required in separators (decanters) downstream the reactor.

- To increase conversion and yield by simultaneous extraction of glycerol produced during transesterification reaction.

Why use LLFC in biodiesel production?

- Because biodiesel production is mainly a heterogeneous reaction requiring dispersion of alcohol rich phase into ester rich-phase

- Because smaller the droplet size higher the residence time in decanters and higher energy consumption

- Because chemical equilibria limit biodiesel yield. Thus several reaction stages are required to accomplish glycerol free and bonded specification

Technologies assessed

- LLFR operated in co-current
  - 2003-2006
- LLFR operated in counter-current
  - 2007-2011
- LLFR operated in co-current using a PES HFM
  - 2012-2016

General methodology

Modeling, design and construction of the experimental setup

Experimental assessing of the setup

Adjust ingmodel parameters according to experimental results

What is going to be kept constant?

The catalyst: sodium methoxide

The alcohol: methanol

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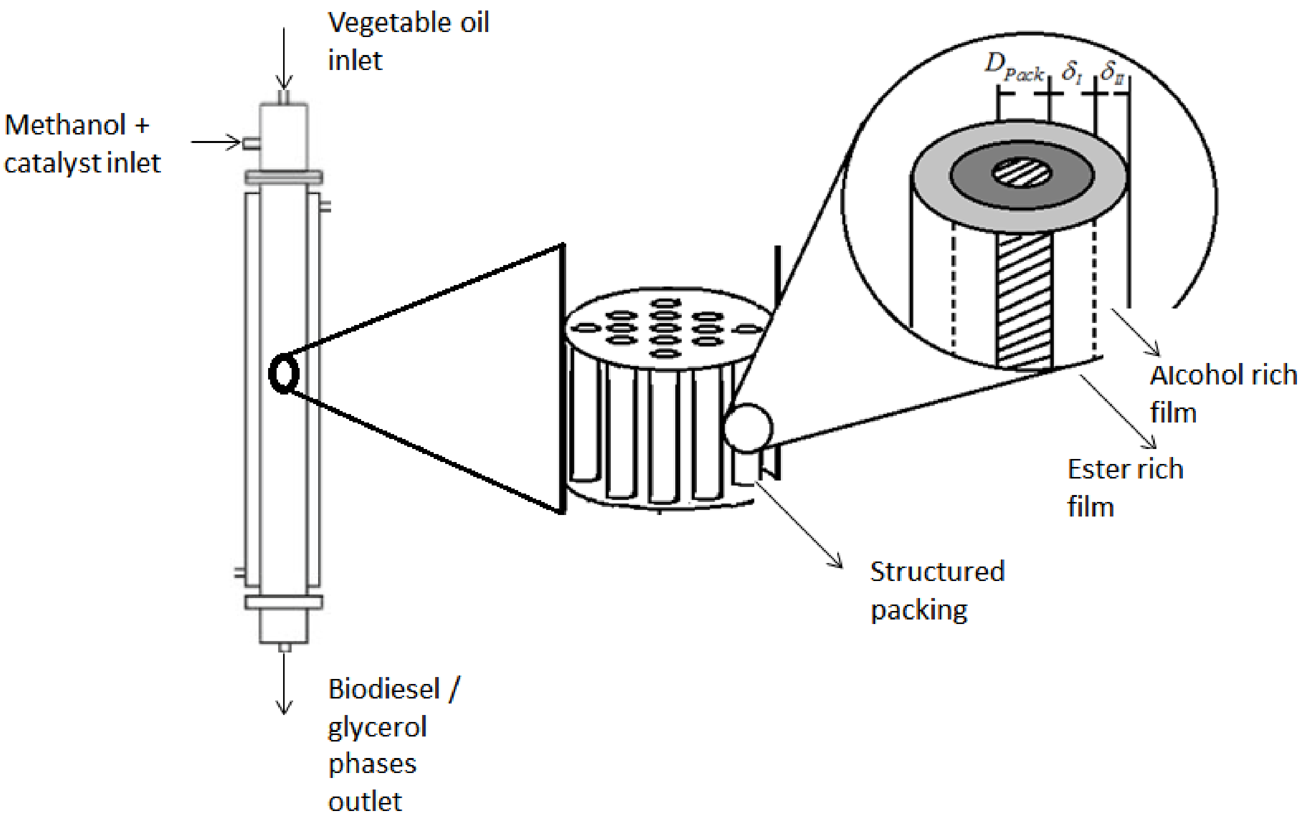
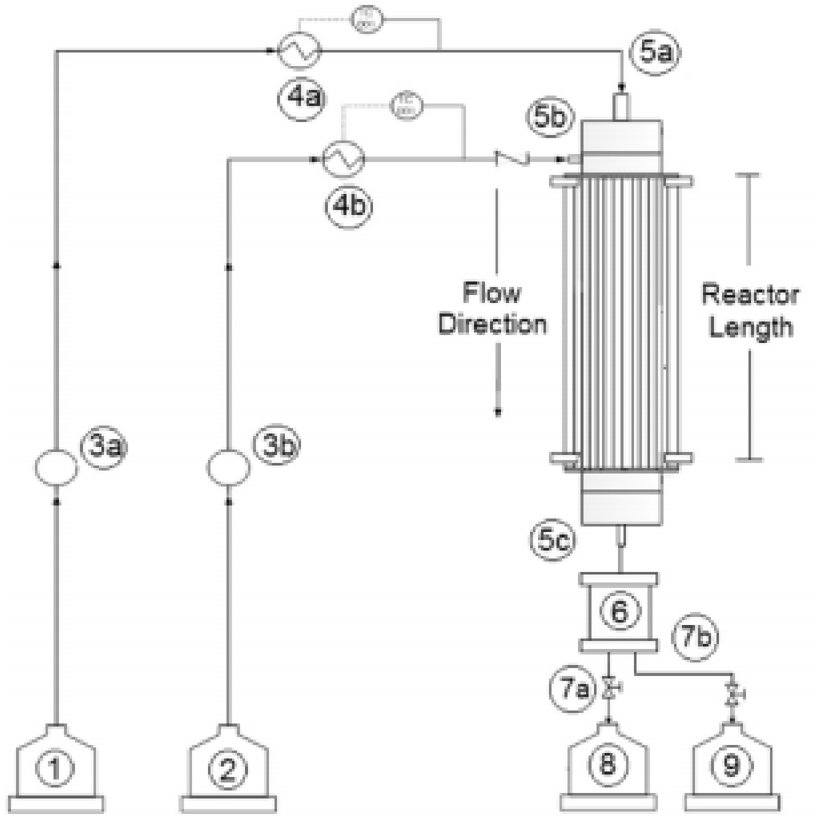
Biodiesel production in LLFR operated in co-current



M.A. Noriega, P.C. Narváez, J.G. Cadavid, A.C. Habert, Modeling of biodiesel production in Liquid-Liquid Film Reactors including mass transfer effects, Fuel Processing Technology, 167, 2017, 524-534. Copyright 2017, with permission from Elsevier

Biodiesel production in LLFR operated in co-current



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Biodiesel production in LLFR operated in co-current

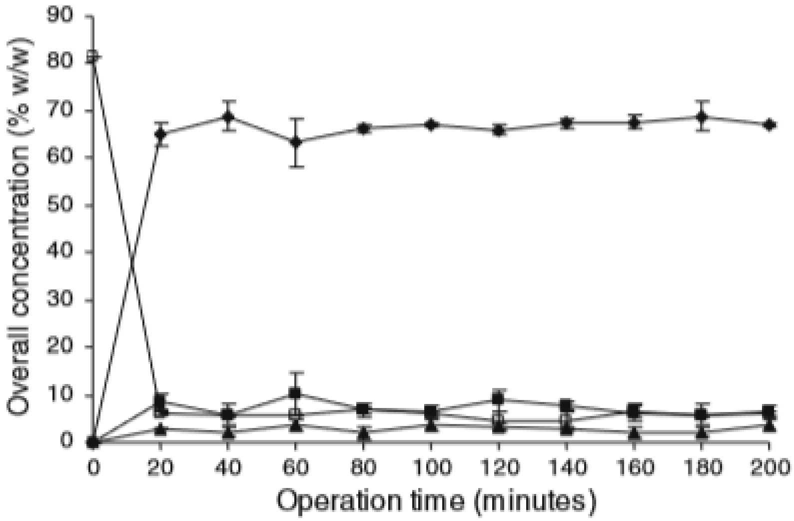

Fig. 3 Overall concentration of palm oil, methyl esters, monoglycerides and diglycerides at the outlet of the LLFR of L/L_{max} 1.0, during the palm oil methanolysis. Palm oil flow rate 27.0 g min^{-1}, methanol to oil molar ratio 6:1, temperature 60 °C, 1 wt.% NaOH based on palm oil. (Filled diamond) methyl esters; (filled square) monoglycerides; (filled triangle) diglycerides; (square) palm oil

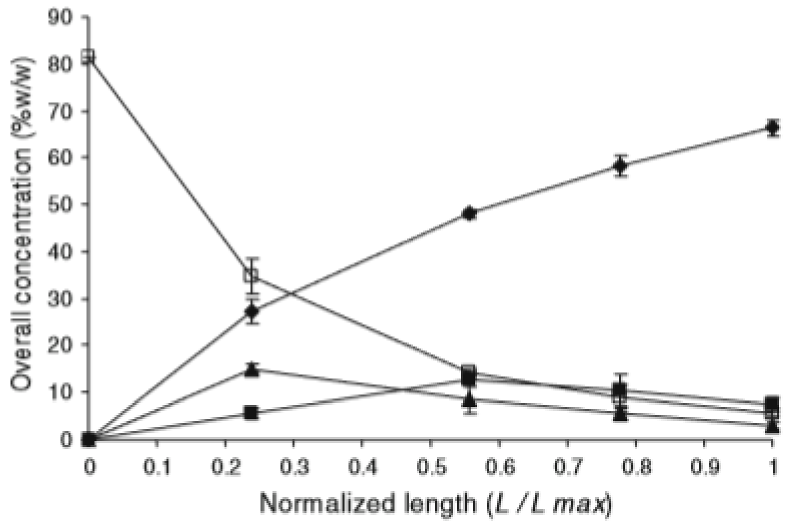

Fig. 4 The effect of the LLFR length on the overall concentration of some feedstock and products during palm oil methanolysis. Palm oil flow rate 27.0 g min^{-1}, methanol to oil molar ratio 6:1, temperature 60 °C, 1 wt.% NaOH based on palm oil. (Filled diamond) methyl esters; (filled square) monoglycerides; (filled square) diglycerides; (square) palm oil. Experimental data correspond to the steady state behavior of the reactor

Narváez PC, Sánchez FJ, Godoy-Silva RD. 2009. Continuous methanolysis of palm oil using a liquid-liquid film reactor, Journal of American Oil Chemists' Society, 86: 343-352.

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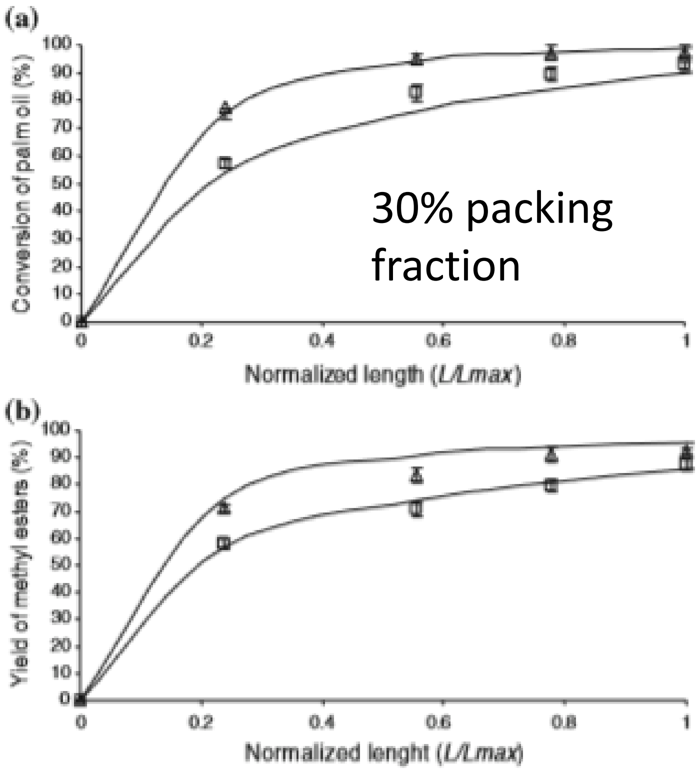
Biodiesel production in LLFR operated in co-current



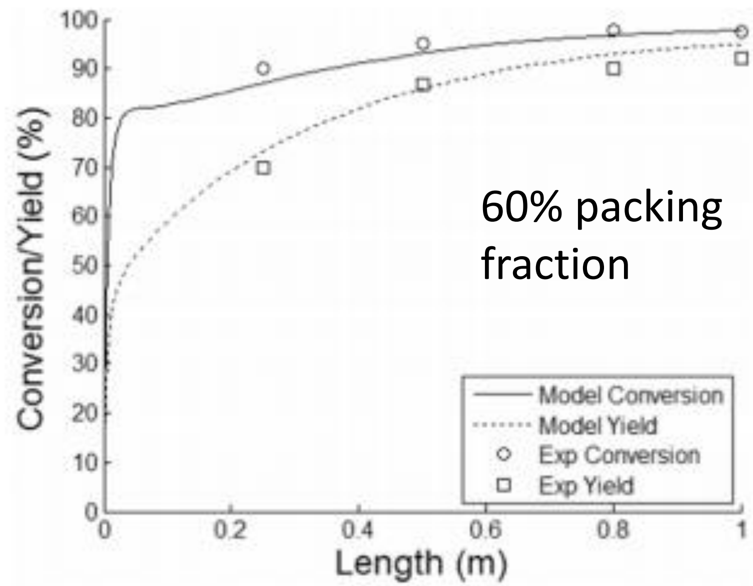


Fig. 10. Reactor length effect on the conversion and FAME yield. VO flow rate 40 g min^{-1} and a_C of 5333 m^{-1}.

Biodiesel production in LLFR operated in co-current increasing packing fraction

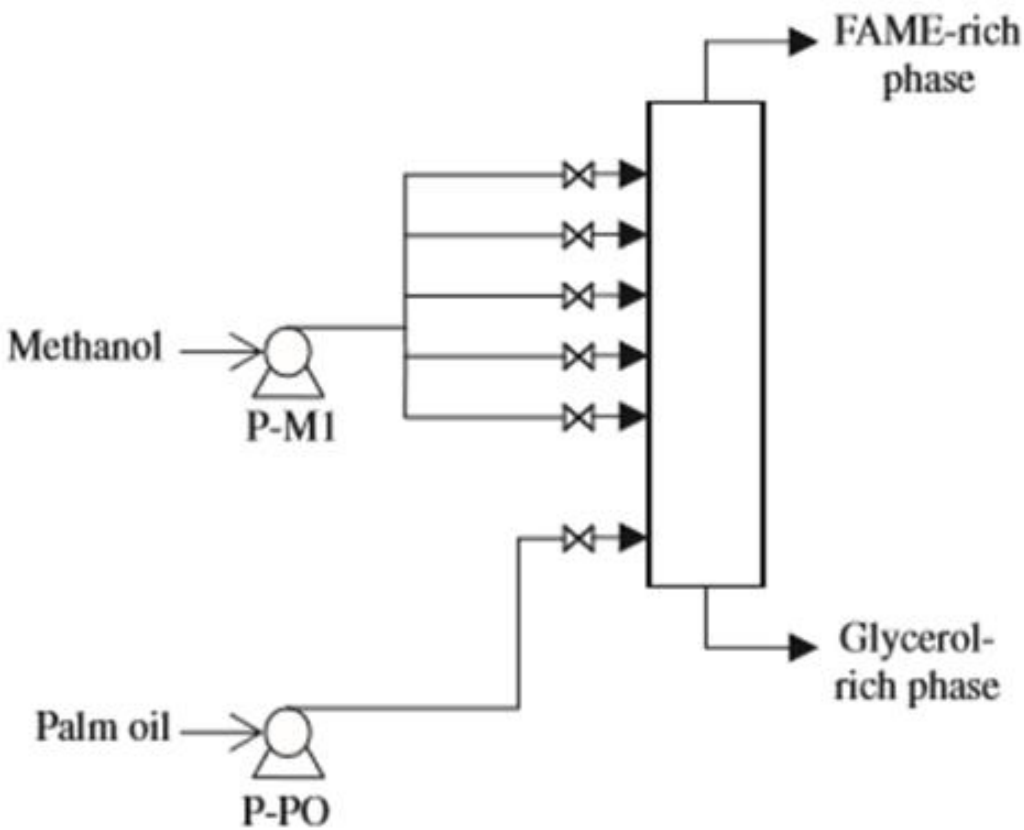
Table 4
Productivity of biodiesel from soybean oil obtained for LLFR and for BSTR at 55 °C, using NaOH as catalyst (1%wt.).

Variable	BSTR [31]	LLFR [30]	LLFR (this work)	LLFR with decanter (this work)
Conversion (%)	99.9	97.5	99.5	99.9
Yield (%)	97.1	92.2	95.1	97.2
Productivity $\left(\frac{m^3 FAME}{h \cdot m^3 reactor}\right)$	0.3	1.2	3.5	2.5
Flow rate (g/min)	N.A[a]	9	40	40
Packing surface to volume (a_c, m^{-1})	N.A[a]	444	5333	5333

[a] Not applicable.

M.A. Noriega, P.C. Narváez, J.G. Cadavid, A.C. Habert, Modeling of biodiesel production in Liquid-Liquid Film Reactors including mass transfer effects, Fuel Processing Technology, 167, 2017, 524-534, Copyright 2017, with permission from Elsevier.

Biodiesel production in LLFR operated in counter-current



Cadavid JG, Godoy-Silva RD, Narváez PC, Camargo M, Fonteix C.2013. Biodiesel production in a counter-current reactive extraction column: Modelling, parametric identification and optimization, Chemical Engineering Journal, 228: 717-723, Copyright 2013, with permission from Elsevier

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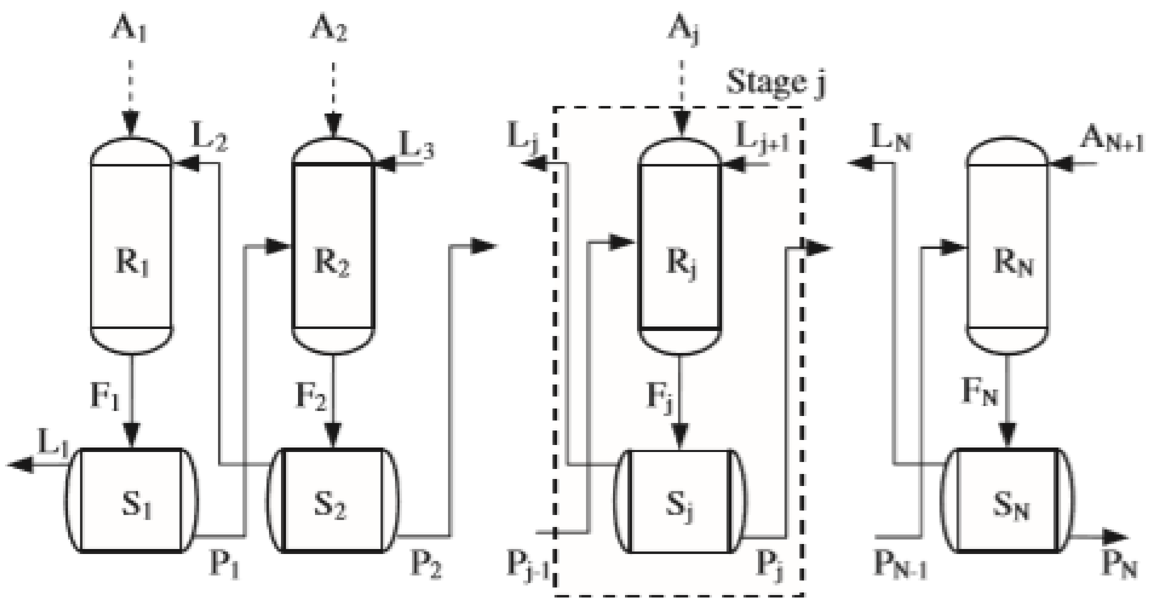
Biodiesel production in LLFR operated in counter-current



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Biodiesel production in LLFR operated in counter-current

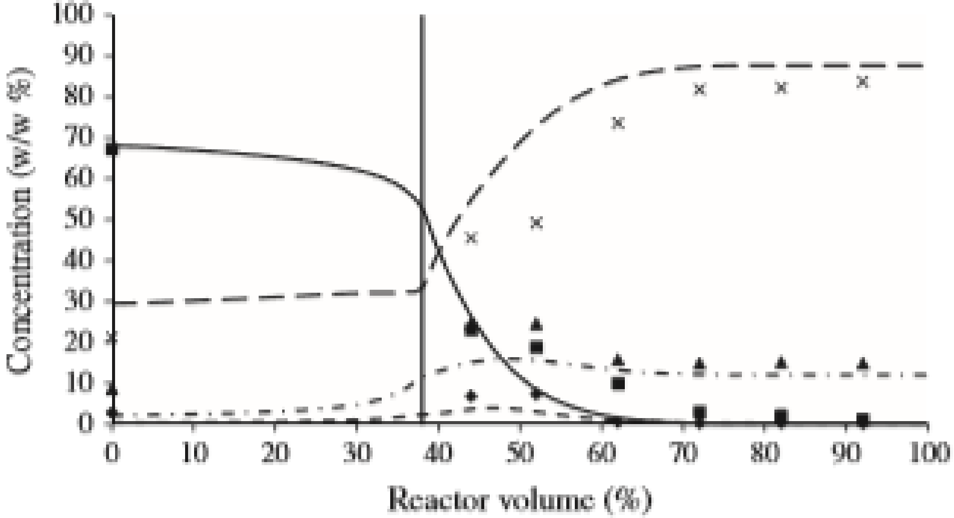

Fig. 5. Biodiesel-rich phase experimental and predicted concentrations during biodiesel production using reactive extraction. Palm oil mass flow rate 32.9 g min^{-1}, methanol to palm oil molar ratio 3.7, methanol feeding length 38% (vertical line). Experimental data: (■) FAME, (♦) MG, (▲) DG, (×) TG. Model predictions: (—) FAME, (---) MG, (-·-·-) DG, (— — —) TG.

Cadavid JG, Godoy-Silva RD, Narváez PC, Camargo M, Fonteix C.2013. Biodiesel production in a counter-current reactive extraction column: Modelling, parametric identification and optimization, Chemical Engineering Journal, 228: 717-723, Copyright 2013, with permission from Elsevier

Biodiesel production in LLFR operated in counter-current

Table 6

Comparison of productivity between counter-current, co-current and batch processes at 60 °C, using NaOH as catalyst (1 wt.% based on palm oil weight or mass flow rate).

Variable	Process		
	Counter-current	Co-current	Batch
Palm oil mass flow rate ($g\ min^{-1}$)	50	50	50[a]
Methanol to palm oil molar ratio	8:1	10:1	12:1
Palm oil conversion (%)	99.7	99.4	99.9
Yield to FAME (%)	99.9	97.2	98.3
Productivity (m^3 of FAME $m^{-3}\ h^{-1}$)	1.8	1.2	0.3

[a] In this case the variables are palm oil mass and reaction time. The reactor volume is evaluated from the reaction mass.

Cadavid JG, Godoy-Silva RD, Narváez PC, Camargo M, Fonteix C.2013. Biodiesel production in a counter-current reactive extraction column: Modelling, parametric identification and optimization, Chemical Engineering Journal, 228: 717-723, Copyright 2013, with permission from Elsevier

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Biodiesel production in LLFR operated in co-current and hollow fiber membranes

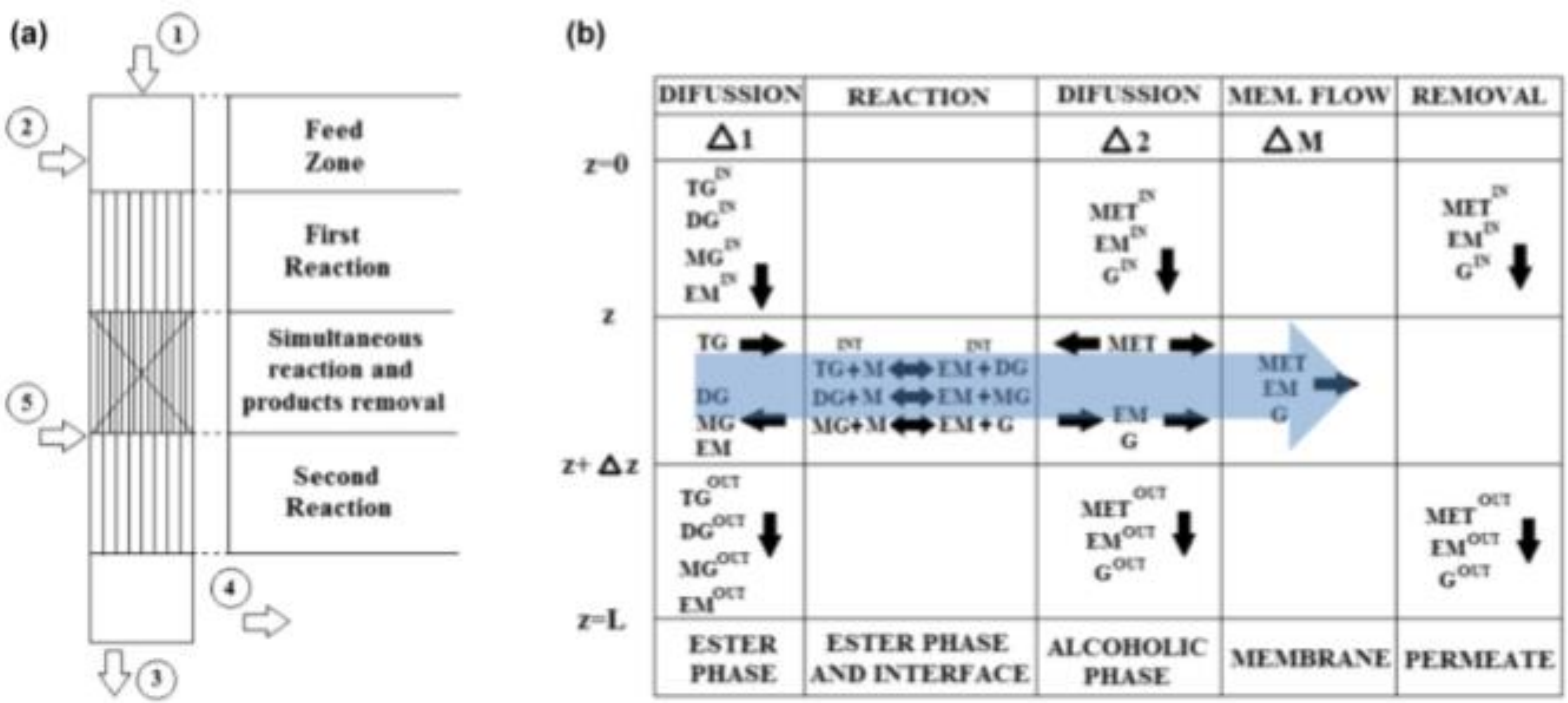

Fig. 1. a) Schematic representation of the LLFRM. b) Schematic transport model in the LLFRM.

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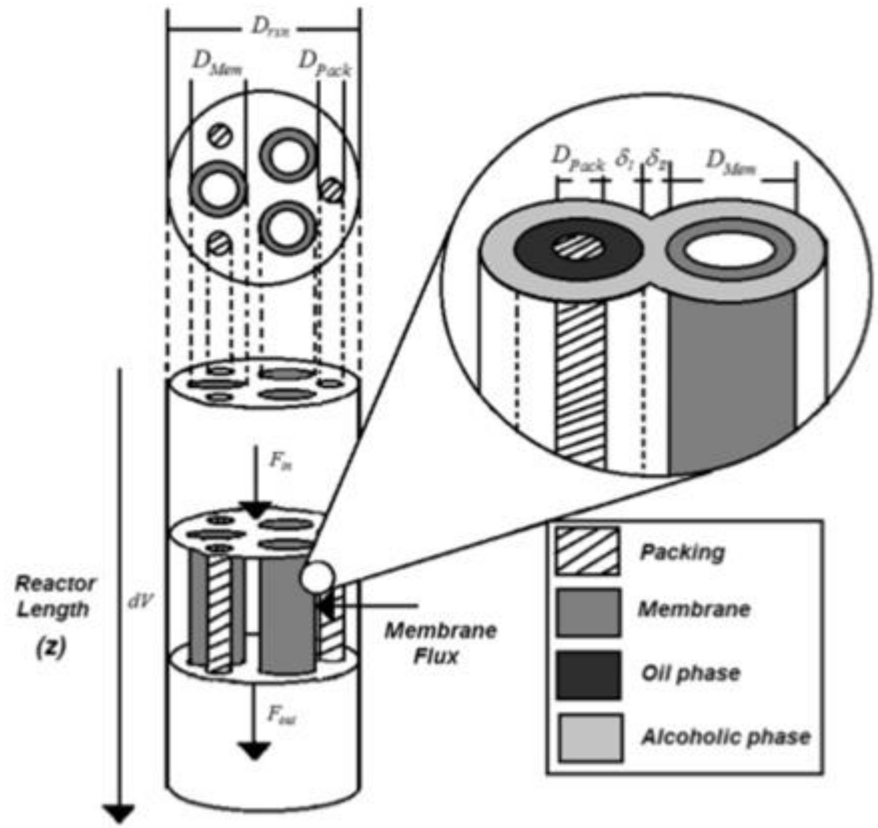
Biodiesel production in LLFR operated in co-current and hollow fiber membranes



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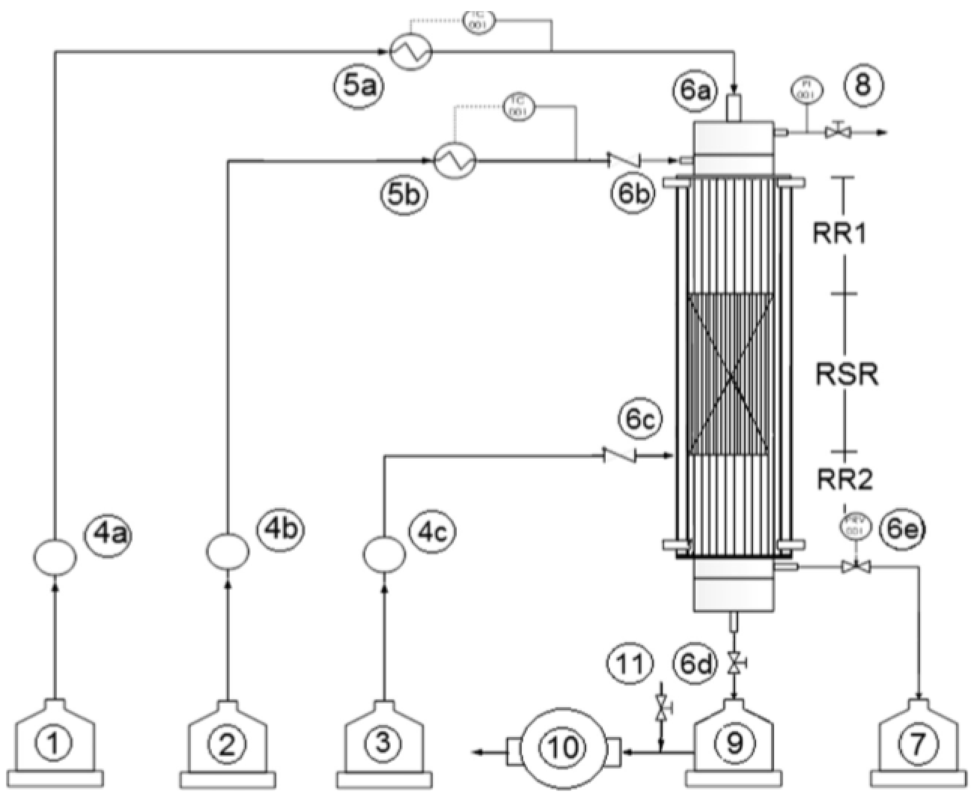

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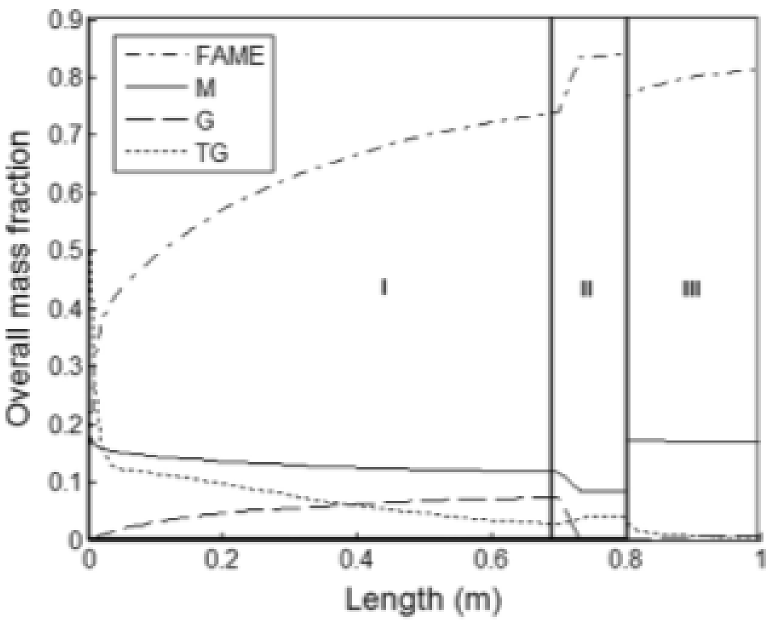

Fig. 6. Performance of the LLFRM over the reactor length as predicted by the model. Temperature 55 °C, Catalyst concentration 1%wt, VO flow rate 20 g min−1, 9:1 methanol to oil molar ratio and 33% Lateral methanol.

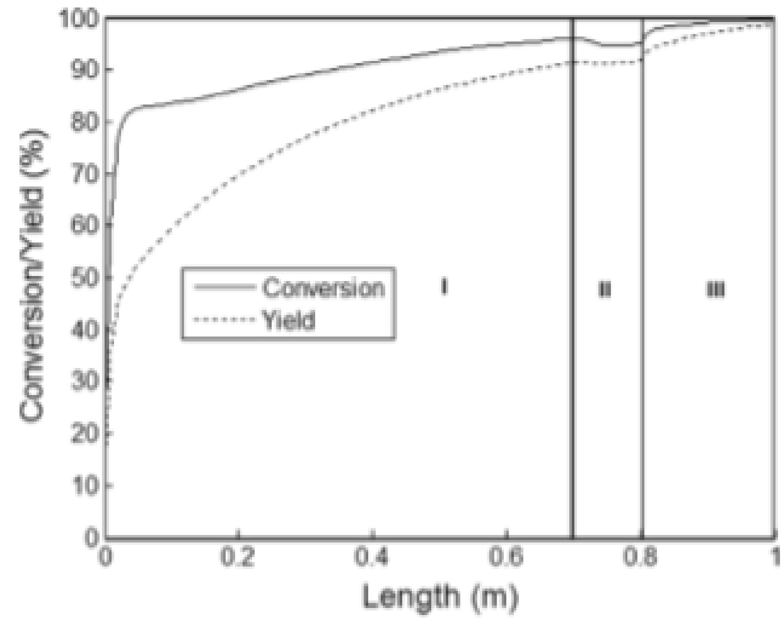

Fig. 7. Model prediction of conversion and FAME yield in an LLFRM. Temperature 55 °C, Catalyst concentration 1%wt, VO flow rate 20 g min^{-1}, 9:1 methanol to oil molar ratio and 33% Lateral methanol [46].

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Biodiesel production in LLFR operated in co-current and hollow fiber membranes

Table 4
Productivity of biodiesel from soybean oil obtained for LLFR, LLFRM, and CSTR at 55 °C, using NaOH as catalyst (1%wt).

Variable	CSTR	LLFR with decanter [47]	LLFR [47]	LLFRM (This work)
Conversion (%)	99.9	99.5	99.9	99.7
Yield (%)	97.1	95.1	97.2	99.3
Productivity $\left(\frac{m^3 FAME}{h \cdot m^3 reactor}\right)$	0.35	3.5	2.5	3.5
Required Stages	2	1	1	1

Conclusion

It is possible to produce biodiesel accomplishing specifications defined in product standards using LLFR operated in two different configurations: counter-current and co-current using HFM implementing only one reaction step, reducing separation time and, as a consequence, increasing process productivity. In co-current two reaction steps are required.

The highest productivity was obtained for the LLFR operated in co-current (with and without membranes).