Estimation of Mass Transfer limitation in Heterogeneous Catalyzed Reaction for Biodiesel Production

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Abstract

In the present study, calculation for turn over frequency and internal and external mass transfer limitations are made for the given kinetics of biodiesel production reaction using Karanja oil as non-edible oil source and Amberlyst15 as heterogeneous acid catalyst. Reaction kinetics are affected by reaction temperature, order of reaction, methanol to oil ratio for Amberlyst15 solid phase catalyst (catalyst active site 4.7×10^{-3} mol/g). Weisz-Prater criterion for internal diffusion and Mears criterion for external diffusion are used to predict the mass transfer limitations for different order and temperature of the reaction. There was no mass transfer limitation was found in biodiesel reaction with Amberlyst15 catalyst for different reaction conditions.

Keywords: Weisz-Prater criterion; Mears criterion; Turn over frequency; Amberlyst15; Mass Transfer; Biodiesel

Introduction

Production of Biodiesel can be done by transesterification and esterification reaction with homogeneous and heterogenous catalyst [1]. Homogeneous catalyzed biodiesel production is much faster than heterogeneous catalyzed biodiesel production [2]. Due to single phase reactions, fast homogeneous reactions are associated with less mass transfer limitation. Biodiesel can be produced by transesterification and esterification reactions using

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heterogeneous catalysts, but at a very slow rate [1, 2]. Plant oil containing high free fatty acid used acid solid phase catalyst [3]. Most of the study used Amberlyst15 as solid phase catalyst with esterification process [4,5,6,7,8]. In heterogenous catalyst active site of catalyst is very important characteristics for any type of reaction. Active site is mainly dependent on turn over number of solid catalysts. Turnover number (TON) refers to how many moles of substrate a catalyst can convert before becoming inactive. [9,10,13] TOF is used to refer to the turnover rate per unit time, with active site represented by mol/g catalyst[9,10]. There are several mass transfer restrictions that apply to heterogeneous catalysts, including diffusion, adsorption, and desorption. In the past, studies had been conducted on reaction kinetics for without caring about the mass transfer limitation [11,12].

In the current study mass transfer limitation are highlighted for the different reaction conditions of given kinetics in the earlier published work [11,12].

Material and Methods

The current mass transfer limitation study is done for the Amberlyst 15 catalyzed biodiesel reaction using Karanja as plant oil. The reaction operating condition was initially selected as Methanol to oil ratio= 6:1, Catalyst amount 45 g, Reaction mixture volume 341 ml. Aberlyst15 had the Catalyst active site 4.7×10^{-3} mol/g.

General Procedure

Reaction kinetics expression for the biodiesel production reaction was reported as power law model used for estimating the kinetic parameters The rate of consumption of the glyceride, -r_{TG} was related to the concentration of glycerides, C_{TG}, by the following equation[4,5,6]

$$-r_{TG} = k_m C_{TG}^n \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad \text{[eq. 1]}$$

where, k_m was the rate constant at a mean reaction temperature of T_m, n was order of reaction Weisz-Prater criterion for internal diffusion for n^{th} order reaction was estimated by the expression [6]

$$C_{wp} = \frac{-r_{TG} R^2 \left(\frac{n+1}{2}\right)}{D_e C_{AS}} \qquad \text{[eq.2]}$$

$C_{wp} < 0.25$ no internal mass transfer limitation

Mears criterion for external diffusion was estimated by [6]

$$= \frac{-r_{TG} R n}{K_c C_{AS}} \qquad \text{[eq.3]}$$

Value < 0.15 no external mass transfer limitation

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Result and discussion

The biodiesel production from the karanja oil by using Amberlyst15 as a solid phase catalyst had been discussed earlier [4, 5, 6]. The kinetic study with the Amberlyst15 catalyst were well defined in the previous studies [4,5,6]. The same result data was taken for the calculation of TON. The assumed operating condition are shown in Table 1

Methanol to oil ratio= 6:1	Activation Energy (E/R) = 6606
Reaction temperature = 333 K	Order of reaction=2.3
Oil concentration = 0.8288 mol/l	Catalyst amount = 45 g
Reaction rate constant = 0.2	Reaction mixture volume =341 ml
Catalyst amount = 45 g	Catalyst active site: 4.7×10^{-3} mol/g

Table 1 Calculation for turn over frequency for operating conditions.

The calculation for Turn Over Number for Amberlyst15 solid phase catalyst.

having Active sites: 4.7×10^{-3} mol/g

catalyst active site concentration in reaction mixture:

$= 4.7 \times 10^{-3} \times 45 \times 1000/341$ mL

$= 0.62$ mol/L

TOF = rate/ catalyst concentration [9,10]

At 333 K the value of the rate was 0.0157 mol/l.h

$$- r_{TG} = 0.0157 \frac{mol}{L.h}$$

TOF $= 0.0157/(0.62 \times 3600)$
      $= 7.03 \times 10^{-6}$ sec^{-1}
Similarly, TOF was calculated at different temperature

The internal mass transfer limitation calculation was done by Weisz-Prater criterion and Mears criterion for external diffusion,

Weisz-Prater criterion

$$C_{wp} = \frac{- r_{TG} R^2 (\frac{n+1}{2})}{D_e C_{AS}}$$

the required values were calculated for operating condition as shown in table 1 as follows

The kinetic expression was

$$- r_{TG} = k_m C_{TG}^n \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right]$$ [eq.4]

$$- r_{TG} = 0.2(0.8288)^{2.3} \exp\left[-6606\left(\frac{1}{333} - \frac{1}{273}\right)\right]$$

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$$-r_{TG} = 0.0157 \frac{mol}{L.h}$$

Effective diffusivity (De)

$$D_e = \frac{D_{AB} \Phi_p \sigma_c}{\tau}$$

Where for spherical particle $\phi_p= 0.4$, $\sigma_c=0.8$, $\tau= 1.44$

Molecular diffusivity (DAB) for liquid phase system

$$D_{AB} = \frac{117.3x10^{-18}(\phi M_B)^{0.5}T}{\mu v_A^{0.6}}$$ [eq.5]

For methanol and oil system

$\phi=1.9$, T=393K,

$\mu= 69.6x\ 10^{-6}\ m^2/s$, $v_A= 37.3x10^3$, $M_B=32$

from eq.5

D_{AB} $= 117.3x10^{-18}(1.9x32)^{0.5}\ x393/(63.33x10^{-3}x0.138)$

      $=4.11x10^{-11}\ m^2/s$

from eq.4

De= $9.3x10^{-10}\ m^2/s$

Calculation for mass transfer coefficient (K_c)

Reynolds no. given by **$N_{Re}=Da^2N\rho/\mu$**

D_a =diameter of the particle

$D_a=5\ x10^{-2}$ m, N=950 rpm, $\rho=0.91$ kg/lit, $\mu= 69.9x10^{-6}$ Kg.m/s

$N_{Re} = (5\ x10^{-2})^2x950x0.91\ /(69.9x10^{-6}x60)$

      $= 5.15X10^2$

      $= 515$

$$K_c = \frac{2D_{AB}}{D_p} + 0.31N_{SC}^{-2/3}(\frac{\Delta\rho\mu_c g}{\rho_c^2})^{1/3}$$ [eq.6]   [9 K]

N_{Sc}   **$=\mu/\rho D_{AB}$**

      $= 69.6\ x10^{-6}/4.11x10^{-11}$

      $= 16.9x10^5$

$$K_c = \frac{2x4.11x10^{-11}}{6x10^{-4}} + 0.31x(16.9x10^5)^{-2/3}(\frac{(0.92-0.61)x63.3x10^{-3}x9.8}{0.92^2})^{1/3}$$

$= 1.48x10^{-6}$ m/s

Mass transfer limitation was checked at various given conditions as temperature 393 K and assumed order of the reaction as first, second and third.

Case 1: Mass transfer limitation check at 393 K

At 393 K the value of the rate was 0.329 mol/l.h

$$-r_{TG} = 0.329 \frac{mol}{l.h}$$

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TOF $= 0.329/(0.62 \times 3600)$
      $= 1.47 \times 10^{-4} \ \text{sec}^{-1}$

Weisz-prater criterion for internal diffusion at 393 K for first order system

C_{wp} $= 0.329 \times (3 \times 10^{-4})^2 / (9.3 \times 10^{-10} \times 0.8288 \times 3600)$
      $= 1.06 \times 10^{-2} << 0.25$

      Therefore, no internal mass transfer limitation occured at 393 K

Weisz-prater criterion for internal diffusion at 393 K for second order system

      C_{wp} $= 0.329 \times (3 \times 10^{-4})^{2 \times} 1.5 / (9.3 \times 10^{-10} \times 0.8288 \times 3600)$
        $1.59 \times 10^{-2} << 0.25$

      Therefore, no internal mass transfer limitation occured at 393 K

Weisz-prater criterion for internal diffusion at 393 K for third order system

      C_{wp} $= 0.329 \times (3 \times 10^{-4})^{2 \times} 2 / (9.3 \times 10^{-10} \times 0.8288 \times 3600)$
        $2.12 \times 10^{-2} << 0.25$

      Therefore, no internal mass transfer limitation occured at 393 K

Mears criterion for external diffusion at 393K

$= 0.329 \times 3 \times 10^{-4} \times 2.3 / (1.48 \times 10^{-6} \times 0.8288 \times 3600)$
$= 5.\ 14 \times 10^{-2}$
$= 5.\ 14 \times 10^{-2} << 0.15$

Therefore, no external mass transfer limitation occured at 393 K

The above calculation shown that for any order at temperature 393 K the reaction did not correspond to any internal and external mass transfer limitation.

Now, the same observation was done for kinetics study at temperature 373 K

The calculation was done at 373 K at given operating condition.

Case 2: Internal Mass transfer limitation checked at 373 K

      Calculation for TOF

$$-r_{TG} = 0.129 \frac{mol}{l.h}$$

TOF $= 0.129/(0.62 \times 3600)$
      $5.78 \times 10^{-4} \ \text{sec}^{-1}$

Weisz-prater criterion for internal diffusion for first order system at 373 K

C_{wp} $= 0.129 \times (3 \times 10^{-4})^2 / (9.3 \times 10^{-10} \times 0.8288 \times 3600)$
      $= 4.18 \times 10^{-3} << 0.25$

Therefore, no internal mass transfer limitation occurred at 373 K

Weisz-prater criterion for internal diffusion for second order system at 373 K

C_{wp} $= 0.129 \times (3 \times 10^{-4})^2 \times 1.5 / (9.3 \times 10^{-10} \times 0.8288 \times 3600)$
      $= 6.27 \times 10^{-3} << 0.25$

Therefore, no internal mass transfer limitation occurred at 373 K

Weisz-prater criterion for internal diffusion for Third order system at 373 K

C_{wp} $= 0.129 \times (3 \times 10^{-4})^2 \times 2 / (9.3 \times 10^{-10} \times 0.8288 \times 3600)$
      $= 8.36 \times 10^{-3} << 0.25$

Therefore, no internal mass transfer limitation occured at 373 K

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Mears criterion was checked for external diffusion at 373K

$= 0.129 \times 3 \times 10^{-4} \times 2.3/(1.48 \times 10^{-6} \times 0.8288 \times 3600)$

$= 6.71 \times 10^{-3}$ $<<0.15$

Therefore, No external mass transfer limitation occurred at 373 K

Furthermore, the mass Transfer limitation was checked at given kinetic condition at 353 K

Case 3: Internal Mass transfer limitation checked at 353 K

$$-r_{TG} = 0.048 \frac{mol}{l.h}$$

TOF $= 0.048/(0.62 \times 3600)$

$= 2.15 \times 10^{-5} \sec^{-1}$

Weisz-prater criterion for internal diffusion for first order system at 353 K

C_{wp} $= 0.048 \times (3 \times 10^{-4})^2/ (9.3 \times 10^{-10} \times 0.8288 \times 3600)$

$= 1.55 \times 10^{-3} <<0.25$

Therefore, no internal mass transfer limitation occurred at 353 K

Weisz-prater criterion for internal diffusion for second order system at 353 K

C_{wp} $= 0.048 \times (3 \times 10^{-4})^2 \times 1.5/ (9.3 \times 10^{-10} \times 0.8288 \times 3600)$

$= 2.325 \times 10^{-3} <<0.25$

Therefore, no internal mass transfer limitation occured at 353 K

Weisz-prater criterion for internal diffusion for third order system at 353 K

C_{wp} $= 0.048 \times (3 \times 10^{-4})^2 \times 2/ (9.3 \times 10^{-10} \times 0.8288 \times 3600)$

$= 3.1 \times 10^{-3} <<0.25$

Therefore, no internal mass transfer limitation occurred at 353 K

Mears criterion used for external diffusion at 353K

$= 0.0.048 \times 3 \times 10^{-4} \times 2.3/(1.48 \times 10^{-6} \times 0.8288 \times 3600)$

$= 5.14 \times 10^{-3}$ $<<0.15$

Therefore, no external mass transfer limitation occurred at 353 K

Conclusion

The calculation for the Internal and external mass transfer limitation was done for the given kinetic data. Results are shown in the given table 2. There was no mass transfer limitation was observed at all the given temperatures. The reaction was mainly effected by the reaction parameters and operating conditions.

Temperature (K)	Order of the reaction	Weisz-prater criterion (Internal mass transfer)	Mears criterion (External mass transfer)	TOF (s^{-1})
353	I	1.55×10^{-3}	5.14×10^{-3}	2.15×10^{-5}
	II	1.325×10^{-3}		
	III	3.1×10^{-3}		
373	I	4.18×10^{-3}	6.71×10^{-3}	5.78×10^{-5}
	II	6.27×10^{-3}		
	III	8.36×10^{-3}		

393	I	1.06×10^{-2}	5.14×10^{-2}	1.47×10^{-4}
	II	1.59×10^{-2}		
	III	2.12×10^{-2}		

Table 2: Summary of the information at different temperature

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