Synthesis of Reactor Networks for Methyl Ester Production

Nurul Fitriah Nasir, Wan Ramli Wan Daud, Siti Kartom Kamarudin, and Zahira Yaakob

Abstract—The main objective of this study is to determine the reactor configurations for biodiesel production through attainable region method. The systematic design method is practically used for determining reactor configurations that will produce the optimal product. Kinetic model for biodiesel production was developed for Plug-Flow Reactor, PFR and Continuous Stirred-Tank Reactor, CSTR. The model was solved in MATLAB and subsequently applied in the attainable region method to determine the reactor structure of two different biodiesel feedstock; waste sunflower oil and rapeseed oil. The results indicate that a CSTR is an optimal reactor with maximum conversion of triglyceride.

Index Terms—Attainable region, biodiesel, kinetic, reactor.
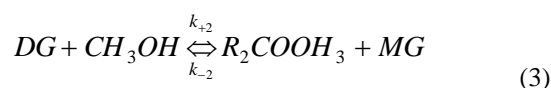
I. INTRODUCTION

One of the most significant steps after development and determination of the structure of a chemical system and the kinetics is to find a suitable reactor which promises a complete process. The synthesis of reactor network in chemical production can be carried out by using a graphical method or by superstructure optimization approaches [1]. This systematic design generation method is called attainable region method and was originated by Horn (1964) [2]. This method determines the area of accessibility involves in several steps such as selection of basic processes, define and vector drawing process, building the region, interpret the boundaries and find the optimal value.

For biodiesel production, the overall reaction is:

$$TG + 3CH_3OH \overset{catalyst}{\Longleftrightarrow} 3RCOOH_3 + GL \tag{1}$$

The stepwise reaction that occurs during the reaction process are listed as follow:

$$TG + CH_3OH \overset{k_{+1}}{\underset{k_{-1}}{\Longleftrightarrow}} R_1COOH_3 + DG \tag{2}$$

$$DG + CH_3OH \overset{k_{+2}}{\underset{k_{-2}}{\Longleftrightarrow}} R_2COOH_3 + MG \tag{3}$$

$$MG + CH_3OH \overset{k_{+3}}{\underset{k_{-3}}{\Longleftrightarrow}} R_3COOH_3 + GL \tag{4}$$

where *TG, DG, MG, GL, RCOOH₃, CH₃OH* and k_i are triglyceride, diglyceride, monoglyceride, glycerol, ester, methanol, and reaction rate constants of each reaction, respectively. This paper aims to determine the reactor structure that yields the optimal methyl esters derived from two different feedstock by attainable region method.

II. METHODOLOGY

A. Attainable Region Method

To observe the path of a plug flow reactor (PFR) with a variable residence time and a fixed triglyceride's feed and methyl ester's feed, the following ordinary differential equations have to be solved from the feed point.

$$-\frac{dC_T}{dt} = k_{+1}C_TC_A - k_{-1}C_DC_{E1} \tag{5}$$

$$-\frac{dC_D}{dt} = -\left(k_{+1}C_TC_A - k_{-1}C_DC_{E1} - k_{+2}C_DC_A + k_{-2}C_MC_{E2}\right) \tag{6}$$

$$-\frac{dC_M}{dt} = -\left(k_{+2}C_DC_A - k_{-2}C_MC_{E2} - k_{+3}C_MC_A + k_{-3}C_GC_{E3}\right) \tag{7}$$

$$-\frac{dC_{E1}}{dt} = -\left(k_{+1}C_TC_A - k_{-1}C_DC_{E1}\right) \tag{8}$$

$$-\frac{dC_{E2}}{dt} = -\left(k_{+2}C_DC_A - k_{-2}C_MC_{E2}\right) \tag{9}$$

$$-\frac{dC_{E3}}{dt} = -\left(k_{+3}C_MC_A - k_{-3}C_GC_{E3}\right) \tag{10}$$

$$-\frac{dC_A}{dt} = k_{+1}C_TC_A - k_{-1}C_DC_{E1} + k_{+2}C_DC_A - k_{-2}C_MC_{E2} + k_{+3}C_MC_A - k_{-3}C_GC_{E3} \tag{11}$$

$$-\frac{dC_G}{dt} = -\left(k_{+3}C_MC_A - k_{-3}C_GC_{E3}\right) \tag{12}$$

where $C_T, C_A, C_D, C_M, C_{E1}, C_{E2}, C_{E3}, C_G$ are the concentration of triglyceride, methanol, diglyceride, monoglyceride, methyl ester 1, methyl ester 2, methyl ester 3 and glycerol, respectively. Published reaction rate constants ($k_{+1} - k_{-3}$) are listed in Table I.

TABLE I: REACTION RATE CONSTANTS [3].

Reaction rate constants (l/mol. min)	Waste Sunflower Oil	Rapeseed Oil
k_{+1}	0.0772	0.0879
k_{-1}	0.1680	0.4777
k_{+2}	0.0972	0.1555
k_{-2}	0.0265	0.1396
k_{+3}	0.0670	0.7478
k_{-3}	0.0088	0.0061

Equations (6) to (12) is solved numerically using a 4th order Runge-Kutta algorithm, which is available in MATLAB. The solution generates the molar concentrations of all species, C_i, as functions of the design variables, i.e. the conversion of the limiting reactant, TG, and the molar ratio of the excess methanol, A. The attainable region for the biodiesel reaction is constructed by first plotting a PFR trajectory from the feed point, continuing to the complete conversion of triglyceride, which is the plot of concentration of the main product, methyl ester against concentration of the limiting reactant, TG, obtained from the solution of Equations (6) to (12). A candidate attainable region is found whenever the PFR plot formed a convex region. In addition, a straight line representing the mixing of product and feed is drawn to fill the non-convex parts of the trajectory. A CSTR trajectory is then constructed to see if the region can be extended. To construct the trajectory, the kinetic model of CSTR needs to be solved first.

The kinetic model for continuous stirred tank reactor (CSTR) is straightforward. The stoichiometric mole balance of each species in a CSTR using the reaction kinetics in Equation (2) to (4) yields a set of non-linear equations in Equations (13) to (20).

$$C_{To} - C_T = \frac{V}{F_T}\left(k_{+1}C_T C_A - k_{-1}C_D C_{E1}\right) = \tau\left(k_{+1}C_T C_A - k_{-1}C_D C_{E1}\right)$$
(13)

$$C_{Do} - C_D = -\tau\left(k_{+1}C_T C_A - k_{-1}C_D C_{E1} - k_{+2}C_D C_A + k_{-2}C_M C_{E2}\right)$$
(14)

$$C_{Mo} - C_M = -\tau\left(k_{+2}C_D C_A - k_{-2}C_M C_{E2} - k_{+3}C_M C_A + k_{-3}C_G C_{E3}\right)$$
(15)

$$C_{E1o} - C_{E1} = -\tau\left(k_{+1}C_T C_A - k_{-1}C_D C_{E1}\right)$$
(16)

$$C_{E2o} - C_{E2} = -\tau\left(k_{+2}C_D C_A - k_{-2}C_M C_{E2}\right)$$
(17)

$$C_{E3o} - C_{E3} = -\tau\left(k_{+3}C_M C_A - k_{-3}C_G C_{E3}\right)$$
(18)

$$C_{Ao} - C_A = \tau\left(\begin{array}{c} k_{+1}C_T C_A - k_{-1}C_D C_{E1} + k_{+2}C_D C_A - k_{-2}C_M C_{E2} + \\ k_{+3}C_M C_A - k_{-3}C_G C_{E3} \end{array}\right)$$
(19)

$$C_{Go} - C_G = -\tau\left(k_{+3}C_M C_A - k_{-3}C_G C_{E3}\right)$$
(20)

Again, CSTR multiple NLE (13) to (20) is solved numerically using MATLAB. The solution generates the molar concentrations of all species, C_i, as functions of the design variables, i.e. the conversion of the limiting reactant, TG, and the molar ratio of the excess variable, A. The plot of the concentration of ME against the conversion or the concentration of the limiting reactant, TG forms the CSTR trajectory. Subsequently, the trajectory is checked to see if the attainable region can be extended. Furthermore, a linear arc is plotted on the CSTR trajectory to ensure it remains convex. An additional PFR trajectory is drawn from the point where the mixing line meets the CSTR trajectory to further extend the attainable region [4, 5]. The same procedure was carried out for determining the suitable reactor for the production of biodiesel from waste sunflower oil and rapeseed oil.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the result of attainable region plot of PFR obtained from waste sunflower oil. The plot shows non-convex part, consequently a straight line AEB that represents a mixing line is needed to fill the non-convex parts of the trajectory. This forms the candidate attainable region. By evaluating the rate vectors (r_T/r_E) along the line, it is found that there are rate vectors at point E that point out of the candidate attainable region. These findings suggest that an additional CSTR trajectory is required.

The CSTR trajectory was drawn starting from the point of the convex hull that extends the region the most. In this case, it is the feed point. From Figure 2, it was noted that the CSTR trajectory also forms a non-convex region thus requires a line segment AC to fill the non-convex portion. At point C, it is apparent that the CSTR trajectory has reached the equilibrium. The result from the attainable region plot has revealed that two different reactor structures lying on the attainable region boundary. The line segment AC represents a CSTR with bypass and point C represents a CSTR.
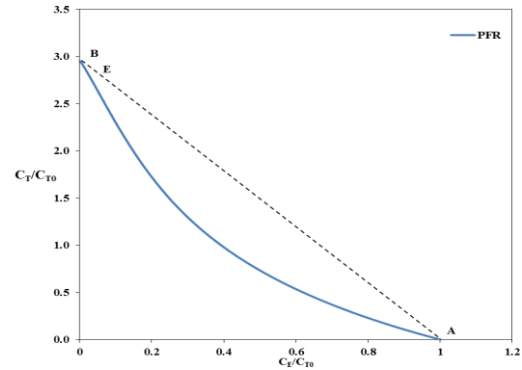

Fig. 1. Initial PFR profile with convex hull for waste sunflower oil.
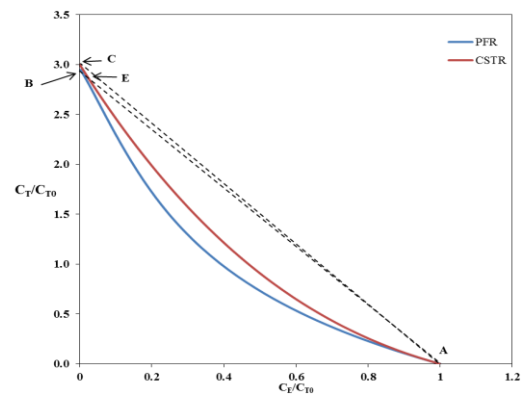

Fig. 2. PFR and CSTR profiles with convex hull for waste sunflower oil.

Fig. 3 presents the PFR profiles obtained from attainable region plot of methyl ester derived from rapeseed oil. The plot also had shown a non-convex region of PFR trajectory. Therefore, a straight line AEB was drawn to fill the non-convex parts of the trajectory thus constitutes a candidate of attainable region. Again, it is found at point E that the rate vectors were point out at the candidate attainable region. This result suggests an additional CSTR trajectory.
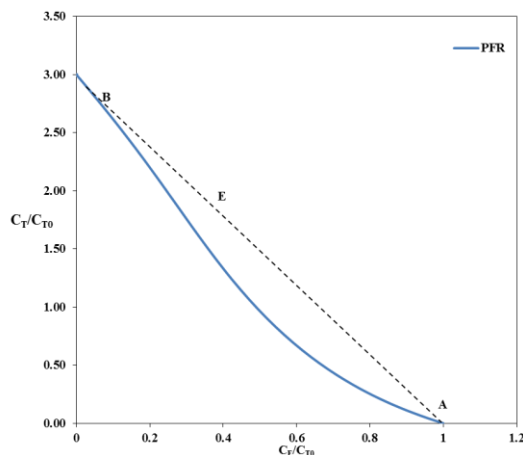

Fig. 3. Initial PFR profile with convex hull for rapeseed oil.

The CSTR trajectory was drawn from the feed point generates Figure 4. As configured in the graph, the CSTR trajectory also forms a non-convex region thus requires a line segment AC to fill the non-convex portion. Again, the CSTR trajectory has reached the equilibrium at point C. The result from the attainable region plot of biodiesel from rapeseed oil has shown that two different reactor structures lying on the attainable region boundary. The line segment AC represents a CSTR with bypass and point C represents a CSTR. Note that an additional PFR trajectory is unnecessary as the CSTR plot has achieved the most expandable region.

The findings from the attainable region method corroborate the research conducted by Darnoko and Cherian (2000), Leevijit et al. (2008) and Komers et al. (2010) [6-8]. For production of methyl ester especially from the feedstock studied, a CSTR was found to be a suitable reactor that gives complete triglycerides conversion. However, for waste oil, an additional esterification reactor is required for reducing the free fatty acid level content.
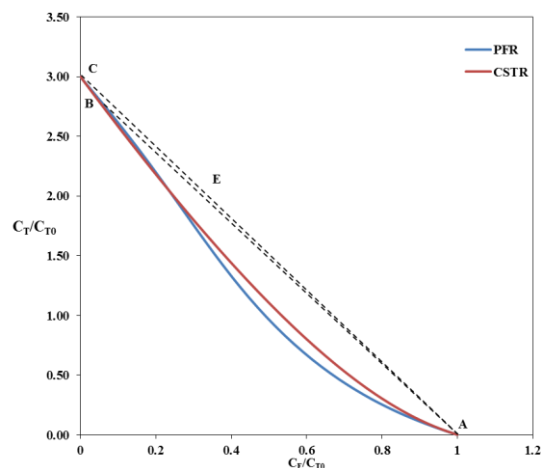

Fig. 4. PFR and CSTR profiles and convex hull for rapeseed oil.

IV. CONCLUSION

The current study was carried out to determine the reactor structure of methyl ester production derived from two different types of feedstock. Attainable region method has provided an opportunity to consider different reactor types in order to produce a maximum conversion of methyl ester by plotting the reactor trajectories. Both type of biodiesel investigated has shown that a CSTR is an ideal reactor that can be considered for selection.

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