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Novel Dynamic Cleaning Model for Cyclic Operation of Biodiesel Membrane Reactors

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A membrane reactor produces high-quality biodiesel by combining both reaction and separation in a single unit. However, the reactor has disadvantages such as high operating expense and reduced efficiency over time due to membrane fouling. To solve this issue, frequent cleaning with physical and chemical methods is required. Membrane cleaning contributes to the reactor's operating cost to a large extent, including energy, chemicals and even production loss. Although there have been studies undertaken focusing on improving membrane cleaning, optimizing the performance of the membrane reactor in biodiesel production has received limited attention. In this work, a novel membrane cleaning model is presented and used to optimize the membrane reactor efficiency in terms of biodiesel yield and cleaning costs. The model captures the dynamic states of reversible and irreversible membrane fouling during the cleaning process. It is further used to evaluate the effects of backwashing and chemical cleaning on the membrane reactor. The results show that the number of backwashes during operation is a crucial factor to improve reactor productivity and reduce the cleaning cost. The membrane reactor's operating time rose 2 to 3 times when the operating period between two backwashes, or an operating cycle, reduced from 70 min to 15 min. The biodiesel yield increased significantly due to the extended operation. However, longer operating time led to an accumulation of more irreversible fouling, which could not be removed by backwashing. The cost of chemical cleaning rose as the irreversible fouling level increased. Regarding the cost-to-yield ratio of the biodiesel reactor, the best operating conditions were found at the operating cycle of 25 minutes between 2 backwashes. Overall, the cleaning model allows the prediction and reduction of the cleaning expense of the membrane reactor, increasing its potential as a biodiesel production technology significantly.

1. Introduction

Biodiesel, which is mainly produced from the transesterification of vegetable oil and alcohol, is a cornerstone of the European Union's (EU) greenhouse gas reduction strategy to reduce the use of fossil fuels in the transport sector. Biodiesel consumption has seen a rise of 6.36 % in EU transportation, from 13.49 Mtoe in 2018 to 14.349 Mtoe in 2019 (Observ'ER, 2020). However, the high price of biodiesel has become the greatest challenge in replace conventional fuels.

To reduce the cost of biodiesel, alternative feedstocks and innovative production processes have been studied. Microalgae are considered a potential candidate for biodiesel production because it does not require agricultural land, can grow very fast, and has a high biodiesel-algae oil yield (96.45 %) (Oprescu et al., 2015). Another promising feedstock is waste cooking oil which is a recyclable material and much cheaper than vegetable oil. However, its production cost is still slightly higher (~ 3.5 %) than fossil-fuel diesel due to additional pre-treatment stages (Liu et al., 2021). The price of biodiesel can also be reduced by applying new technology in both the reaction and separation stages of production. Intensified processes such as reactive separations are interesting processes that have good simulated results compared to traditional processes. However, their utility consumptions are still remarkably high and would need to be reduced before the process can be applied in actual production (Petrescu et al., 2020).

Membrane technology has gone through significant developments in the past decades. It has the potential to improve biofuel production. A membrane reactor produces higher quality biodiesel than traditional reactors due

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to its high conversion rate and selectivity of the desirable product (Cao et al., 2008). Biodiesel production using a membrane reactor requires fewer downstream processing stages than conventional processes (Abdurakhman et al., 2018). The application of membrane technology has economic and environmental benefits in reducing energy consumption, material for equipment, wastewater and the chemicals used in biodiesel production.

However, the fouling which originates from unreacted substances is the main inherent drawback of the membrane reactor and greatly affects the reactor efficiency. To restore membrane efficiency, fouling needs to be frequently removed by physical and chemical methods. Therefore, membrane cleaning is critical (Popović et al., 2010). Although the cleaning cost is driving the operational cost of the membrane reactor (chemical cost, lost productivity, etc.), physical and chemical cleaning procedures are mainly determined from experience without precise prediction of results (Cui and Muralidhara, 2010). Prediction and optimization of membrane reactor cleaning are challenging tasks due to the complex relationship between membrane properties, membrane fouling, and operating conditions (Wang et al., 2014). Research into fouling control and membrane cleaning optimization is urgently needed.

Much research focuses on defining effective cleaning strategies (Kim et al., 2020), fabricating new self-cleaning material (Al-Najar et al., 2021), or developing new technique such as ultrasonic cleaning (Aktij et al., 2020). Although membrane cleaning has been studied extensively, membrane reactors in biodiesel production still lack dedicated research on fouling control and removal.

In this study, a cleaning model of a membrane reactor for biodiesel production has been developed to fill the research gap. The model captures the dynamic states of membrane fouling during the physical and chemical cleaning processes. The cleaning cost, i.e., the cost of energy, chemicals, and production loss, is calculated from the relationship between the fouling level, the cleaning duration, and the utility consumption for cleaning. Consequently, the optimal cleaning conditions can improve membrane reactor efficiency in terms of operating cost and productivity.

2. Membrane cleaning model

The membrane cleaning model can predict the state of cleaning chemical, reversible and irreversible fouling as functions of time, washing flow and chemical inlet concentration. The cleaning model is capable of characterizing the effects of backwashing and chemical cleaning by combining with a membrane reactor model.

2.1 Membrane fouling theory

Membrane fouling mechanism can be categorized into four types: 1) complete pore blocking, 2) standard pore blocking, 3) intermediate pore blocking, and 4) cake filtration (Hermia, 1985). The fouling of a membrane reactor in biodiesel production can be described as the combination of complete pore blocking and cake filtration because the oil droplets are pinned onto pore openings by the filtration pressure and coalesce into the gel-like layer on the membrane surface (Salama et al., 2019). The complexity of fouling makes the task of modelling the dynamic effects of fouling and cleaning on the membrane reactor very difficult.

An effective way to capture the change of fouling during membrane operation and cleaning is using assumptions: 1) the complete pore blocking is irreversible with backwashing and partly irreversible with chemical cleaning, and 2) the cake formation is reversible (Daniel et al., 2011). The relation between permeate flux, J, and the fouling resistance, R_f, is presented as the membrane filtration equation (Daniel et al., 2011):

$$J = \frac{\Delta P}{\mu \cdot R_f} \tag{1}$$

$$R_f = R_m + R_c \tag{2}$$

where R_f is the total fouling resistance of membrane, R_m and R_c are irreversible and reversible fouling resistances, ΔP is the transmembrane pressure and μ is the filtration fluid viscosity. The irreversible fouling resistance is described by Eq(3) which is derived from Hermia's complete blocking filtration law (Daniel et al., 2011).

$$\frac{dR_m}{dt} = k_m \cdot J \cdot R_m^2 \tag{3}$$

where k_m is the effective rate constant associated with the pore-blocking mechanism. The reversible fouling resistance is relating to the cake formation on membrane surface that can be presented as (Daniel et al., 2011):

$$\frac{dR_c}{dt} = k_{c1} \cdot J - k_{c2} \tag{4}$$

where k_{c1} is the proportionality constant relating to the mass (or thickness) of the fouling layer, k_{c2} is relating to the removal rate of the cake layer, which is a character of the crossflow filtration.

2.2 Model development

The membrane cleaning model is developed basing on the relationship of the fouling resistances, the cleaning flow and the reaction between a cleaning chemical and the irreversible fouling material (Zondervan et al., 2007). The fouling state of the membrane $x_f(t)$ is related to the fouling resistance according to:

$$x_f(t) = \frac{R_f(t)}{R_f'} \tag{5}$$

where $R_f(t)$ is the fouling resistance during cleaning at a specified pressure and R'_f is the fouling resistance at the beginning of the cleaning.

Backwashing is commonly used to enhance the permeate flux by periodically removing the reversible fouling. The outlet of the permeate channel is closed, and the permeate is pumped back to the feed channel of the membrane module, thus, lifting the fouling off the membrane surface (Cheryan, 1998). The decay of the reversible fouling state, $x_{f,r}$, is described by:

$$\frac{dx_{f,r}}{dt} = -k_r \cdot F_r \cdot x_{f,r} \tag{6}$$

where k_r is the correlation constant between the removal of fouling layer and fouling resistance and F_r is the dimensionless reversal permeate flow:

$$F_r = \frac{F_{r,in}}{F_{r,ref}} \tag{7}$$

where $F_{r,in}$ and $F_{r,ref}$ are the pumped flow at the inlet of the permeate channel and the reference flow based on the pump capacity.

Chemical cleaning is applied when the irreversible fouling that the backwashing cannot remove reaches a critical level. A typical chemical cleaning process includes physical washing with high-temperature solvent or water and dissolving the foulant with a chemical reaction. The change of irreversible fouling state, $x_{f,ir}$, during the chemical cleaning is represented as (Zondervan et al., 2007):

$$\frac{dx_{f,ir}}{dt} = -k_{ir} \cdot F_{ir} \cdot \left(x_{f,ir} - x_{f,\infty}\right) - r_c \tag{8}$$

Where $x_{f,\infty}$ is the fouling state of the membrane at infinite cleaning time, k_{ir} is the physical washing constant and F_{ir} is the dimensionless washing flow calculated from the inlet flow of the chemical cleaning stream $F_{ir,in}$ and the reference flow $F_{ir,ref}$:

$$F_{ir} = \frac{F_{ir,in}}{F_{ir,ref}} \tag{9}$$

The reaction between the irreversible fouling and cleaning chemical is assumed to be first order. The reaction rate, r_c, is calculated by:

$$r_c = k'_1 \cdot x_c \cdot \left(x_{f,ir} - x_{f,\infty}\right) \tag{10}$$

where k'_1 is the reaction rate constant and x_c is the state of the cleaning chemical which is dimensionless and defined by the concentration of cleaning chemical at the start, $C_{chemical,0}$ and during the cleaning, $C_{chemical}(t)$.

$$x_c(t) = \frac{C_{chemical}(t)}{C_{chemical,0}} \tag{11}$$

The state of the chemical agent during the cleaning process is defined as (Zondervan et al., 2007):

$$\frac{dx_c}{dt} = k_{ir} \cdot F_{ir} \cdot \left(x_{c,in} - x_c\right) - n_c \cdot r_c \tag{12}$$

where $x_{c,in}$ is the state of chemical cleaning at the inlet of membrane module and n_c is a pseudo-stoichiometric constant for the fouling decomposition.

2.3 The cleaning cost

The cost of cleaning can be determined from production loss, energy and chemicals consumption. The cost relating to biodiesel loss during the cleaning time, $Cost_{BD}$, is calculated as:

$$Cost_{BD} = m_{f,av} \cdot t_c \cdot W_{BD} \tag{13}$$

where $m_{f,av}$ is the average mass flow of biodiesel produced from the membrane reactor, t_c is the cleaning duration, and W_{BD} is the price of biodiesel. The energy consumption includes the pumping and heating of cleaning fluid. The cost of energy, C_E, is a function of the washing stream, $F_{ir,in}$, specific pumping energy consumption, E_P, specific heating energy consumption, E_H and cleaning duration, t_c. The energy cost is presented as:

$$Cost_E = F_{ir,in} \cdot t_c \cdot W_E \cdot (E_P + E_H) \tag{14}$$

where W_E is the price of energy. The cost of cleaning chemicals, $Cost_C$, is defined as:

$$Cost_C = F_{ir,in} \cdot t_c \cdot W_C \cdot C_{chemical,in} \tag{15}$$

where W_C is the price of chemical and $C_{chemical,in}$ is the concentration of cleaning chemical at the inlet.

2.4 Model solution

The model above can be used to predict the value reversible and irreversible fouling resistances over time and at the end of a filtration cycle, that will be the initial values of the cleaning model. To solve the model, it is assumed that there is no cake formation at the start of the membrane reactor operation or $R_{c,0}$ = 0 and the initial fouling resistance is the intrinsic membrane resistance which is irreversible or $R_{m,0} = R_{f,0}$. Three constants k_m, k_{c1} and k_{c2} are determined by fitting the filtration equations with experimental data. The filtration equations provide the initial reversible and irreversible resistances to solve the cleaning model. The cleaning model parameters k_r, k_{ir}, k'_1 and n_c can be estimated from experiments and simulation data.

The model is solved with the ODE45 solver of Matlab®. The results of the cleaning model are used to estimate the cleaning time and chemical consumption that contribute to the cleaning cost. The states of fouling after cleaning are the initial condition for a new operation cycle of the membrane reactor. This data can be used to calculate the biodiesel production per cycle by using the membrane reactor model, which is a combination of the filtration equation and component balance of the transesterification process (Huynh and Zondervan, 2021). The effects of backwashing on the membrane reactor's productivity, the operating cycle and irreversible fouling accumulation were reported in the biodiesel reactor model of Huynh and Zondervan (2021).

3. Results and discussion

The model was validated with the experimental data of biodiesel production in a membrane reactor from (Cheng et al. 2012). The constants of the chemical cleaning model were estimated from a cleaning simulation based on an experimental cleaning curve of an ultrafiltration membrane (Zondervan et al., 2007). The model parameters are shown in Table 1 and Table 2.

Table 1: Parameters of filtration equations

Parameter	k_m	k_{c1}	k_{c2}
Filtration equations	1.48×10^{-12}	4.5×10^{14} (m^{-2})	1.03×10^{7} (m^{-1} s^{-1}))

Table 2: Parameters of the cleaning model

Parameter	k_r	k_{ir}	k'_1	n_c
Cleaning model	0.0055 (s^{-1})	1.026×10^{-4} (s^{-1})	0.1415 (s^{-1})	0.4566 (s^{-1})

To determine the chemical cleaning duration, it is assumed that the chemical cleaning will reduce 100 % of irreversible fouling resistance. The inlet flowrate of cleaning fluid is 2 times the normal flowrate of filtration to ensure the removal of foulant, $F_{ir,in}$ = 0.4 L/min. The cleaning chemical is sodium hydroxide 1 % Wt. and the cleaning temperature is 70 °C.

The relationship between the number of backwashes per hour with the irreversible fouling and chemical cleaning duration is shown in the Figure 1(a). The graphs show that more irreversible fouling accumulates with shorter operating cycle or higher number of backwashes per hour, demanding longer chemical cleaning times. However, Figure 1(b) shows that the estimated cleaning cost per tonne of biodiesel is increasing with the increase of operating cycle. The reason is that the biodiesel production rate and the total production time rise with more backwashing occurred during the operation.

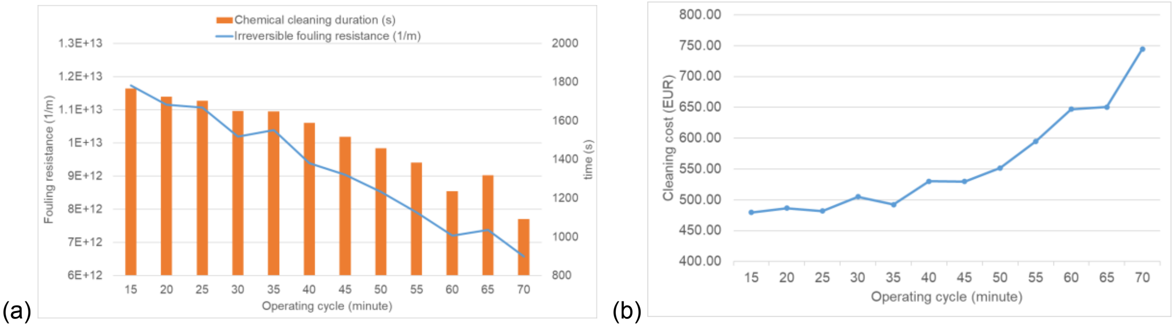

Figure 1: The relation between the backwashing frequency and (a) the irreversible fouling and the chemical cleaning time; (b) the cleaning cost.

The results show that the cleaning cost per t of biodiesel is reduced from 745 to 482 EUR/t by reducing the operating cycle from 70 min to 25 min. However, the cleaning cost of the membrane reactor cannot be reduced further when the operating cycle reduces from 25 min to 15 min or the number of backwashes increases from 2 to 4/h. The biodiesel production rate only slightly increases as compared to the accumulation rate of fouling. This can be explained by the fact that the membrane reactor nearly reaches its capacity limit, which can be risen by increasing the filtration area or using different membrane materials. The prolonged chemical cleaning time will reduce the membrane lifetime.

4. Conclusions

This is the first time a dynamic cleaning model which defines the cleaning and fouling states as functions of time, cleaning flow, reversible and irreversible fouling resistances is applied for the membrane reactor in biodiesel production. The cleaning model is proven that it is an important tool to improve the potential of membrane reactor in biodiesel production by reducing operating cost. In this work, the operating cycle or duration between two backwashes, which balances between cleaning cost and time, and productivity can be determined as 25 min. The cleaning cost per weight of biodiesel produced was reduced 35 % when the operating cycle decreased from 70 min to 25 min. Future work will focus on the effects of different operating and cleaning conditions to further reduce the cleaning cost and raise the membrane reactor's efficiency.

Nomenclature

$C_{chemical,in}$ – chemical inlet concentration, mol/m^3
$Cost_{BD/E/C}$ – cost of biodiesel loss/energy/chemical, EUR
E_P – specific pumping energy, kW/m^3
E_H – specific heating energy, kW/m^3
F_r – backwashing inlet flow, m^3/s
F_{ir} – chemical cleaning flow, m^3/s
J – permeate flux, m^3/(m^2·s)
$m_{f,av}$ – biodiesel average mass flow, kg/s
R_c – reversible fouling resistance, m^{-1}
R_f – fouling resistance, m^{-1}
R_m – irreversible fouling resistance, m^{-1}
t_c – cleaning duration, s
x_f – membrane fouling state, -
x_c – cleaning chemical state, -
$W_{BD/C}$ – price of biodiesel/chemical, EUR/kg
W_E – price of energy, EUR/kW
ΔP – transmembrane pressure, kPa
μ – dynamic viscosity, Pa·s

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