

Advanced Reactor Engineering

Transesterification of Triglycerides to Fatty Acid Methyl Esters

Introduction

Fatty acid methyl esters (FAMES) are extensively used compounds in the industry, but they are perhaps most widely known for their application as biodiesel. In our efforts to phase out fossil fuel based resources such as petroleum and coal, the generation of our energy and materials from renewable and waste resources can be expected to play a larger role. FAMES can be produced through the transesterification of triglycerides (TG) with methanol (MeOH), usually with the use of a homogeneous or heterogeneous catalyst. The reaction scheme for the use of homogeneous NaOH base catalyst is illustrated below in Fig. 1.

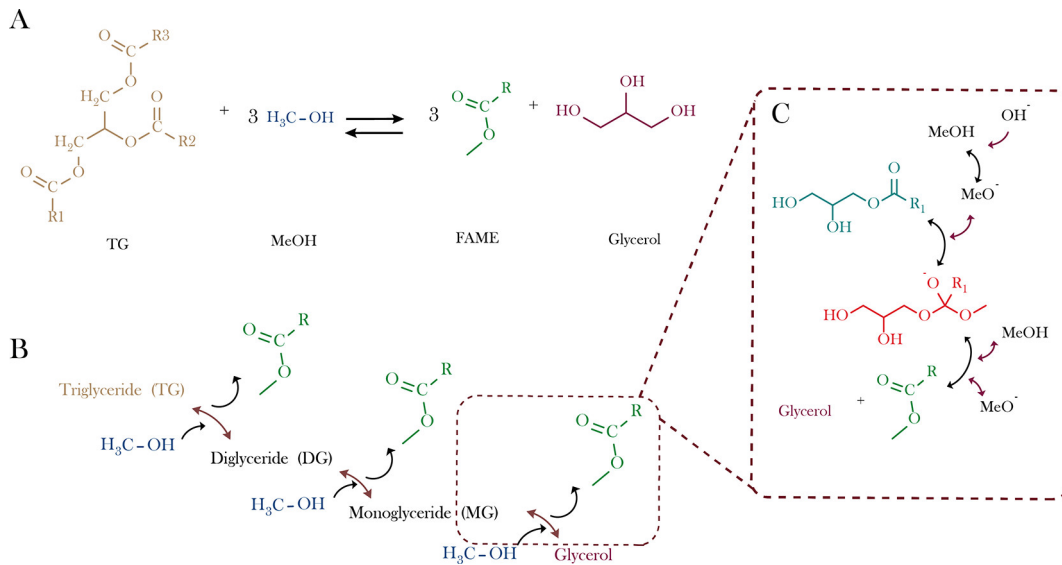


Figure 1: (A) Overall transesterification reaction with MeOH. (B) Intermediate formation of diglyceride (DG) followed by monoglyceride (MG) and finally glycerol (G). (C) Reaction mechanism involving MeOH and NaOH (as catalyst) illustrated for the case of monoglyceride transesterification

The reversible reaction involves the successive formation of diglycerides (DG) and monoglycerides (MG) as intermediates, with each step being a reversible reaction. The catalytic reaction mechanism involves the formation of a tetrahedral intermediate, which is rearranged to form the

products.

Conventionally, batch or continuous stirred tank reactors are often used for the production of FAMEs. However, because of the presence of multiple phases in the system, it can be expected for high kinetic reaction rates that the use of a reactor that can generate a higher amount of specific surface area between the phases will lead to an acceleration of reaction rates through mass transfer intensification.

The rotor-stator spinning disc reactor (RS-SDR) is one such device where high amounts of turbulence can be generated in the system, leading to increased interfacial surface area for multiphase systems. The high turbulence levels are generated in the reactor as a result of the rapid rotation of a disc in a small rotor-stator gap (maximum of a few millimeters). A schematic of the reactor is illustrated in Fig. 2. Furthermore, to improve the productivity of the system, the volume of the overall reactor can be increased by stacking stages. Typically, the radius of the rotor for a single spinning disc reactor is 65 mm. The gap distance is typically 2 mm.

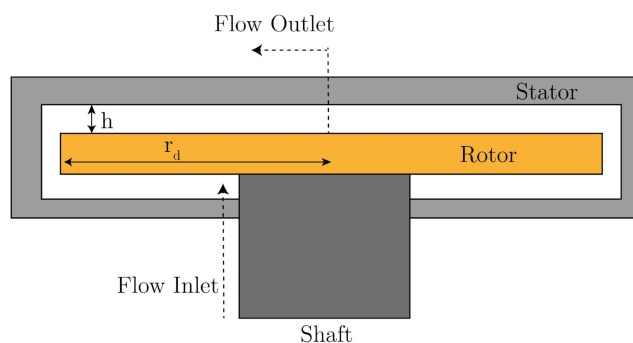


Figure 2: A simple schematic of a rotor–stator spinning disc reactor. The rotor has a radius of r_d and the axial gap is represented in the diagram as h .

Problem Statement

44 million kilos of frying oil are used annually in the Netherlands. If we wish to process this feedstock, i.e. using waste conversion into products to be more sustainable, one option might be to do so in a modular, decentralized fashion. Therefore, the goal of this assignment is to model a spinning disc reactor for the processing of this waste product to useful chemicals. FAMEs are potential feedstock for the production of many surfactants, roughly a 50 billion euro market with the top European producers BASF, Evonik, Nouryon, and Solvay.

First let us consider the case of the homogeneous transesterification reaction. TG is the continuous phase, and the MeOH:TG molar feed ratio is 6:1. The R group of TG can be assumed to be $-C_{15}H_{31}$ (palmitic acid ester). The catalyst, NaOH, is dissolved in MeOH and the amount of catalyst used is 1 wt.%. The volume of a spinning disc stage in the reactor can be chosen as desired,

given that the dimensions of the chosen reactor are close to the values given in the reactor description above (not more than 50% deviation). It is especially important to ensure that the gap distance is not greater than 5 mm. The reactor model can be approximated to be a continuously stirred tank reactor (CSTR) for both phases. Because the catalyst is soluble only in MeOH, the reaction can be modeled as occurring only in the MeOH droplet phase.

Also consider the case of a solid-liquid-liquid reaction. The solid phase consists of sodium metasilicate (Na_2SiO_3) nanoparticles, which act as a catalyst, as it provides Brønsted base sites. The nanoparticles can be considered to be nonporous with the reaction taking place only on the surface of the catalyst. Assume that the Si-O^- Brønsted base is equally active as OH^- .

The nanoparticles are introduced into the system as a slurry along with the TG flow, or they can be coated on the disc. Consider both types of systems for evaluation. The TG is still the continuous phase and the molar ratios described above still hold. For the slurry flow, a maximum of 30 wt% of catalyst can be introduced into the reactor with the TG flow (weight percent based on the TG inflow). The diameter of the nanoparticles is 100 nm; however, particle agglomeration will take place in the reactor. The agglomerates of the nanoparticles have a porosity $\epsilon_A = 0.5$ and a tortuosity $\tau_A = 3$. The size of the agglomerates is determined by the turbulence intensity; agglomerates are broken up until the force by turbulent eddies cannot overcome the van der Waals forces between the particles; the body-body Van der Waals forces are usually expressed by the Hamaker constant. The transesterification reaction in large agglomerates may suffer from internal diffusion limitation.

For the disc-coated system, choose a catalyst layer thickness between 5-400 μm with porosity $\epsilon_A = 0.4$ and tortuosity $\tau_A = 4$, the layer consists entirely of nanoparticles, assume that 80% of the surface area of the nanoparticles is still available after coating. Given the hydrophilic nature of the nanoparticles, it is likely that they will be in the methanol-glycerol phase and that this phase will be present in the coating(!). The reactor model can be approximated as a continuously stirred tank reactor (CSTR) for all mobile phases.

Assume that the density, surface tension and partition coefficients provided are constant across all temperatures and compositions. The viscosity is a function of temperature as specified in Equation 1 and 2. The diffusivity is a function of temperature and viscosity following the correlation of Wilke and Chang (AIChE Journal, Volume 1, 1955), $D/D_{ref} \approx (T/T_{ref})(\mu_{ref}/\mu)$. The reference diffusivity of all components in both phases is given at 50 degrees Celsius in Table 3. The properties of the continuous phase may be used to evaluate the characteristics regarding the spinning disc reactor itself. **The temperature of the reactor can be set to any value you please to optimize the productivity, however ensure that the pressure for the reactor is chosen to be high enough to counter the high vapor pressure of methanol. You may assume ideal behavior of the methanol to calculate the pressure, i.e. activity coefficient equal to 1.**

Assess the effect of the rotation speed on the following parameters: mass transfer rate, droplet size, and energy dissipation rate. Consider how the overall conversion to FAMES is also affected by the rotation speed. There will be a separation unit after the reaction process, however if you maximize the reaction in the RS-SDR, the separation step will have less costs associated with it. Give a final design of the system that also accounts for either the number of stages in the RS-SDR and/or the number of RS-SDRs if you need to process 44 million kilos of frying oil annually with

a reactor unit per 50,000 people, with 16 million total inhabitants in The Netherlands. Conduct a similar analysis for both the coated and slurry systems. Finally, compare the RS-SDR with a conventional reactor (e.g. stirred tank). The dimensions of these reactors can be chosen yourself. Make sure to state your assumptions in different parts of the model and also comment on the assumptions and their impacts. In your conclusions, ensure that you have a discussion on the feasibility of your findings.

Parameters and Correlations

This section provides the parameters and correlations which can be used for completing the assignment. Note that the correlations provided for the spinning disc system are for a single-stage reactor.

The viscosity [Pa s] of the methanol and TG phase as a function of temperature.

$$\ln(\eta_{TG}) = -13.2722 + \frac{2792.919}{T} \quad (1)$$

$$\ln(\eta_{MeOH}) = -11.916 + \frac{1315.706}{T} \quad (2)$$

Assume that the viscosity of both phases is independent of composition.

The energy dissipation rate (E_{dr} [W]) in a RS-SDR can be correlated with the normalized gap distance, G , and the rotational Reynolds number, Re_ω by the following equation:

$$E_{dr} = 5.73 \cdot 10^{-12} G^{-0.14} Re_\omega^{2.12} \quad (3)$$

The normalized gap distance, G and the rotational Reynolds number can be calculated as follows:

$$Re_\omega = \omega r_d^2 \nu^{-1} \quad (4)$$

$$G = h r_d^{-1} \quad (5)$$

Here, ω is the rotation speed in rad s^{-1} (normally in the range of 10-450), r_d the radius of the disc, ν the kinematic viscosity, and h the gap distance.

The kinetic constants for the homogeneous reaction are given in Table 1

k_1 , k_2 , and k_3 represent forward reactions, while k_4 , k_5 , and k_6 represent backward reactions.

The mass transfer coefficient from the continuous phase to the dispersed phase can be described by the correlation of Sano, assuming completely suspended particles/droplets:

$$Sh = [2 + 0.4(\epsilon d_{avg}^4 \nu^{-3})^{1/4} Sc^{1/3}] \quad (6)$$

with ϵ the specific energy dissipation rate (W/kg) calculated from the energy dissipation rate, volume of the reactor and density of the continuous phase; ρ_d the density of the droplet; S_a the specific surface area of the droplet (assuming perfectly spherical particles); and d_{avg} the average droplet size.

Table 1: **Reaction Rate Constants for the Transesterification Reaction with Methanol and 1 wt% NaOH as homogeneous catalyst**

Rate Constants ($\text{L mol}^{-1} \text{ min}^{-1}$)		Kinetic Constants Evaluated at 50° C	E_A [kJ mol^{-1}]
k_1		0.1172	85.9
k_2		0.1680	82.8
k_3		0.1372	17.3
k_4		0.0565	90.3
k_5		0.0870	38.1
k_6		0.018	13.5

Table 2: **Reaction Rate Constants and the corresponding reaction**

Rate Constants	Corresponding Reaction
k_1	TG+ MEOH \rightarrow FAME + DG
k_2	DG+ MEOH \rightarrow FAME + MG
k_3	MG+ MEOH \rightarrow FAME + G
k_4	TG + MEOH \leftarrow FAME + DG
k_5	DG + MEOH \leftarrow FAME + MG
k_6	MG+ MEOH \leftarrow FAME + G

The average droplet size in the RS-SDR can be obtained from the work of Kolmogorov and Hinze who provide the droplet size as a function of the energy dissipation rate:

$$d_{avg} = 0.062 \left(\frac{\sigma}{\rho_c} \right)^{3/5} \epsilon^{-2/5} h \quad (7)$$

Where, σ is the surface tension of the dispersed phase and ρ_c is the density of the continuous phase.

The particle agglomeration can also be described using the energy dissipation rate using the following equation:

$$d_{ag} = d_p + 5.76 \cdot 10^3 \epsilon^{-2/5} d_p \quad (8)$$

The constants required for the evaluation are provided in Table 3. The partition coefficients are a simplification to avoid evaluation of complete Non-Random Two Liquid thermodynamic activity models for the two phases. The partition coefficients m_i are defined for component i as:

$$m_i = \left(\frac{C_i^{TG}}{C_i^{MeOH}} \right)^{eq} \quad (9)$$

Table 3: **Some relevant constants required for evaluation**

Constant	Values	Units
σ	22.5	mN m ⁻¹
ρ_{MeOH}	792	kg m ⁻³
ρ_{TG}	918.8	kg m ⁻³
D_{TG}^{TG}	6.1×10^{-11}	m ² s ⁻¹
D_{DG}^{TG}	5.8×10^{-11}	m ² s ⁻¹
D_{MG}^{TG}	5.7×10^{-11}	m ² s ⁻¹
D_G^{TG}	5.6×10^{-11}	m ² s ⁻¹
D_{FAME}^{TG}	3.7×10^{-11}	m ² s ⁻¹
D_{MeOH}^{TG}	7.8×10^{-10}	m ² s ⁻¹
D_{TG}^{MeOH}	9.2×10^{-11}	m ² s ⁻¹
D_{DG}^{MeOH}	8.4×10^{-11}	m ² s ⁻¹
D_{MG}^{MeOH}	7.4×10^{-11}	m ² s ⁻¹
D_G^{MeOH}	6.2×10^{-11}	m ² s ⁻¹
D_{FAME}^{MeOH}	4.6×10^{-11}	m ² s ⁻¹
D_{MeOH}^{MeOH}	1.6×10^{-9}	m ² s ⁻¹
m_{TG}	150	m _{MeOH} ³ m _{TG} ⁻³
m_{DG}	105	m _{MeOH} ³ m _{TG} ⁻³
m_{MG}	54	m _{MeOH} ³ m _{TG} ⁻³
m_G	0.0062	m _{MeOH} ³ m _{TG} ⁻³
m_{FAME}	47	m _{MeOH} ³ m _{TG} ⁻³
m_{MeOH}	0.0031	m _{MeOH} ³ m _{TG} ⁻³
$\rho_{Na_2SiO_3}$	$2.61 \cdot 10^3$	kg m ⁻³
Brønsted base surface conc.	$42.8 \cdot 10^3$	mol _{Si-O} m _{Na₂SiO₃} ⁻²

Note: D_{FAME}^{MeOH} means diffusivity of FAME in MeOH phase.

D_{FAME}^{TG} means diffusivity in TG phase.

m_i is the equilibrium ratio of concentration of i in the TG phase over the MEOH phase.