

Laboratory 4: Chemical Equilibrium in Biodiesel Production

Topics Covered

- Forward chemical reactions vs. reverse reactions
- Chemical reactions in equilibrium
- Ways to stimulate a reaction to proceed towards completion
- Chemical reactions involved in biodiesel production

Equipment Needed (per pair or group)

- 250 mL flask and small watch glass or stopper
- 125 mL Erlenmeyer flask and stopper
- Separatory funnel, 250 mL
- Stirring hot plate and magnetic stir bar
- Thermometer
- Aluminum foil
- Weighing scale (accurate to 0.001g)

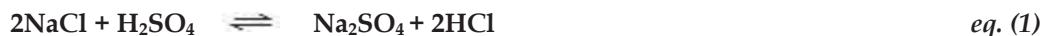
Reagents Needed (per pair or group)

- 20 grams methanol (anhydrous, reagent grade)
- 1 gram potassium hydroxide (as catalyst)
- 100 grams soybean oil (representative molecular weight = 877 g/mol) (can be replaced by canola oil, or other types of virgin vegetable oil)

Background: Introduction to Chemical Equilibrium

Chemical reactions can go forwards and backwards at the same time. Substances in a closed container can react with each other to produce new substances (referred to as the “forward reaction”); these new substances can also react with each other to form the original substances (referred to as the “reverse reaction”).

As a chemical change starts, the quantities of the components on the left side of the reaction equation will decrease, and those on the right side will increase. The eventual results depend on the nature of the overall reaction. A reversible reaction is a reaction in which both the forward and reverse reactions are significant. An example is sodium chloride (NaCl) reacting with sulfuric acid (H_2SO_4) to produce sodium sulfate (Na_2SO_4) and hydrochloric acid (HCl):



Notice that two molecules of NaCl react with one molecule of H₂SO₄ to produce one molecule of Na₂SO₄ and two molecules of HCl. Once sufficient amounts have been produced, Na₂SO₄ will react with HCl to produce NaCl and H₂SO₄. Reversible reactions are commonly written with double arrows pointing in opposite directions, showing that the reaction can proceed in either direction.

Strictly speaking, all chemical reactions are reversible reactions. However, some reactions result in a final product mixture such that the reverse reaction is so insignificant, and the reactant concentrations are at such negligible quantities after reaction, that these reactions are considered irreversible. An example of an irreversible reaction is the reaction between calcium chloride (CaCl₂) and sodium carbonate (Na₂CO₃), which produces calcium carbonate (CaCO₃) and sodium chloride (NaCl):



In this reaction, the product CaCO₃ is a solid that precipitates out to the bottom of the liquid solution container. Its concentration in the solution is so low that it hardly ever reacts with NaCl in solution to form CaCl₂ and Na₂CO₃ again. Therefore, it is generally considered an irreversible reaction. Notice that the equation for this irreversible reaction is indicated by a one-direction arrow.

Given sufficient time, an overall reaction will appear stopped, i.e., the concentrations of reactants and products in the system remain unchanged, although the forward reaction and the reverse reaction may still be going on. The reaction appears stopped because the forward reaction proceeds at the same rate as the reverse reaction. The reaction system at this state is in chemical equilibrium (or in dynamic equilibrium).

Therefore, reversible reactions can be explained from the point of view of chemical equilibrium. A chemical reaction is said to be incomplete, or reversible, when the reaction is in an equilibrium state in which significant quantities of both reactants and products are present. It is said to be complete, or irreversible, when the reaction is in an equilibrium state in which only significant quantities of products are present.

Chemical equilibrium is important in order to predict the reactant conversion rate or the product yield from a chemical reaction. To explain this, a generic chemical reaction occurring in solution (or reaction in liquid phase) with arrows pointing both ways indicates that the overall reaction is reversible, as shown below:



Where: A , B , P , and S are chemical species involved in the reaction, and a , b , p , and s are the stoichiometric coefficients of the corresponding species in the reaction.

The law of mass action explains and predicts the behaviors of chemical reaction solutions in a mathematical form. It describes the rates of forward and reverse reactions in the system, and defines the equilibrium of the overall chemical reaction and the composition of chemical species in the system. The law of mass action states that any chemical change is a competition between a forward reaction and a reverse reaction.

For eq. (1), the rates of reaction (r_A and r_p) can be written as:

$$\text{Rate of forward reaction on reactants: } r_A = k_A \cdot [A]^a \cdot [B]^b \quad \text{eq. (4)}$$

$$\text{Rate of reverse reaction on products: } r_p = k_p \cdot [P]^p \cdot [S]^s \quad \text{eq. (5)}$$

Where: $[A]$, $[B]$, $[P]$, and $[S]$ are the concentrations of chemical species in the reaction; k_A and k_p are the corresponding rate constants.

It is said that a chemical reaction is in equilibrium if the rate of the forward reaction is the same as that of the reverse reaction. When the rate of forward reaction is the same as the rate of reverse reaction (i.e., $r_A = r_p$), it is said that the overall reaction reaches a dynamic equilibrium, i.e., the overall reaction appears to have stopped but is continuing in both directions at the same rate (Fig. 1).

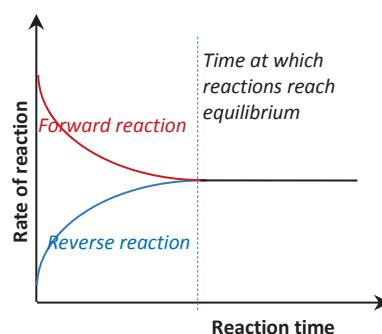


Figure 1. Illustration of forward and reverse reaction at equilibrium.

At the equilibrium point, the concentrations of $[A]$, $[B]$, $[P]$, and $[S]$ remain constant, and an Equilibrium Constant K_{eq} is used to describe the relationship among the concentrations at a given temperature:

$$K_{eq} = \frac{k_A}{k_P} = \frac{[P]^p \cdot [S]^s}{[A]^a \cdot [B]^b} \quad eq. (6)$$

K_{eq} is temperature dependent, and may carry units based on the stoichiometric coefficients of the reaction. For example, in the following reaction,



The value of K_{eq} at 300 K is 4×10^{31} and dimensionless. This value of K_{eq} will decrease to 4×10^{18} if the temperature is increased to 500 K,⁴ which indicates that increasing the temperature of the system favors the reverse reaction or the decomposition of the gaseous product HCl.

When a chemical reaction is at equilibrium, any change of the system process parameters will alter the composition to a new equilibrium state following Le Chatelier's principle. Le Chatelier's principle states that if a change in temperature, pressure, or concentration of chemical species is introduced in a chemical reaction in equilibrium, the reaction system will shift its equilibrium composition in a way that tends to counteract this change of variable. According to Le Chatelier's principle, a reaction system can be affected and then reach a new equilibrium in several ways, such as:

- 1) adding or removing reactants or products from a reaction system
- 2) increasing or decreasing partial pressures of reactants and/or products in a gaseous reaction system, and
- 3) increasing or decreasing the temperature of the reaction system

Generally speaking,

- 1) Adding a chemical species that is neither a reactant nor a product will not affect the chemical equilibrium (if the reaction system is a liquid phase reaction, or the added chemical does not affect the total pressure of the system). For example, a heterogeneous catalyst does not belong to a reaction system. Therefore, adding a catalyst to a system will affect both the forward reaction and the reverse reaction in the same way and reduce the time at which equilibrium is reached, but will not affect the equilibrium constant (i.e., the equilibrium constant remains the same numeric value).

⁴ Chemical Equilibrium at <http://pages.towson.edu/ladon/chemeq.html>. Accessed on July 2, 2012.

- 2) Changing the partial pressure of a gaseous reactant (or a gaseous product) in a gas-phase reaction system of fixed reaction volume is equivalent to changing the concentration of the gaseous reactant (or the gaseous product), and thus will change the chemical equilibrium.

3) Changing the temperature of the reaction system may shift the chemical equilibrium because the temperature may affect the rates of forward and reverse reactions (i.e., k_A and k_p) differently. Note that the temperature affects the rate of reaction based on the Arrhenius' Law: $k_i = k_0 e^{-E/RT}$. Where k_i is the rate of reaction at a given temperature in $kmol/m^3 \cdot s$, k_0 the temperature-independent coefficient in $kmol/m^3 \cdot s$, E the activation energy in $kJ/kmol$, R the universal gas constant of $8.314 \text{ kJ}/\text{kmol} \cdot \text{K}$, and T the given temperature in K.

Background: Transesterification Reaction in Biodiesel production

The biodiesel reaction involves 1 mole of triglyceride (oil or fat) reacting with 3 moles of methanol to produce 3 moles of fatty acid esters (the biodiesel) and 1 mole of glycerol (the byproduct). The reaction is called “transesterification” because it is a process of converting one kind of ester (triglycerides) into another kind (methyl fatty acid esters).

Transesterification is a reversible reaction and will reach equilibrium as the reaction proceeds (Figure 2). Each triglyceride contains three chains of fatty acids connected by a glycerol backbone. To replace the glycerol from these three fatty acids, three moles of methanol are needed, each reacting with one fatty acid.

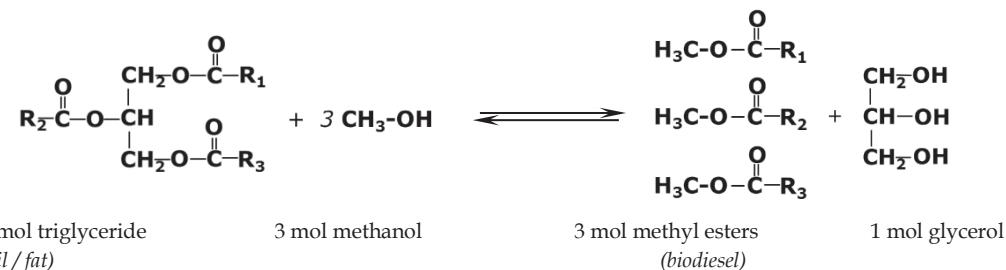


Figure 2. Transesterification of triglycerides with methanol to produce fatty methyl esters.

In Figure 2, each “R” refers to a fatty acid chain. Naturally formed seed oils and animal fats contain triglycerides with even-numbered carbon-chain fatty acids, typically from 16-carbon (or C₁₆ for short) to 22-carbon (or C₂₂ for short). The R₁, R₂, and R₃ can be saturated (i.e., no double bonds), or unsaturated (i.e., with one or more double-bonds), and can be the same type of fatty acid chain or can be totally different. Figure 3 is a graphic model of a triglyceride composed of a saturated palmitic acid (C_{16:0}), an oleic acid of one unsaturated carbon-carbon bond at position 3 (C_{18:1}), and a linoleic acid of two unsaturated carbon-carbon bonds at positions 3 and 6 (C_{18:2}).

Biodiesel Fundamentals for High School Chemistry Classes

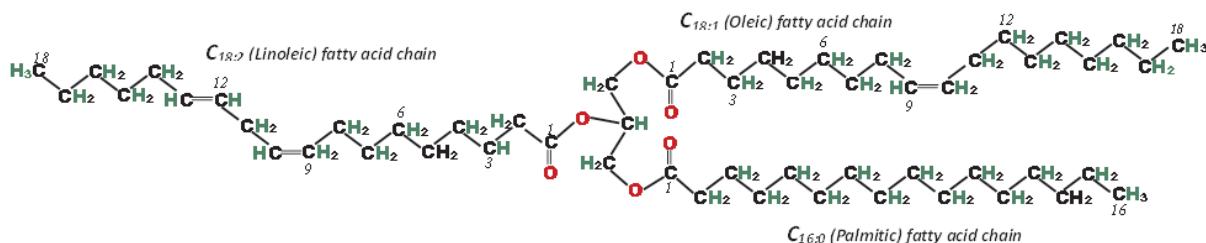


Figure 3. An example of triglyceride structure

The transesterification reaction actually happens in three steps. Each is a reversible reaction with methanol:

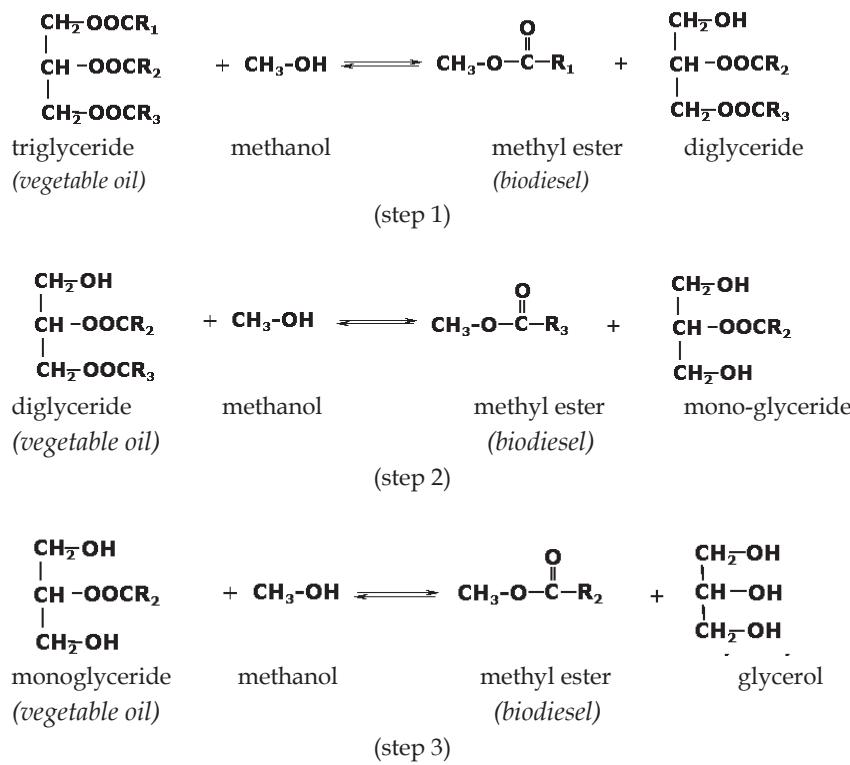


Figure 4. Transesterification of triglycerides with methanol stepwise.

These three reactions do not occur at the same reaction rate, and Step 2 (i.e., the reaction of di-glyceride to mono-glycerides) is the limiting step, as illustrated in Figure 5.

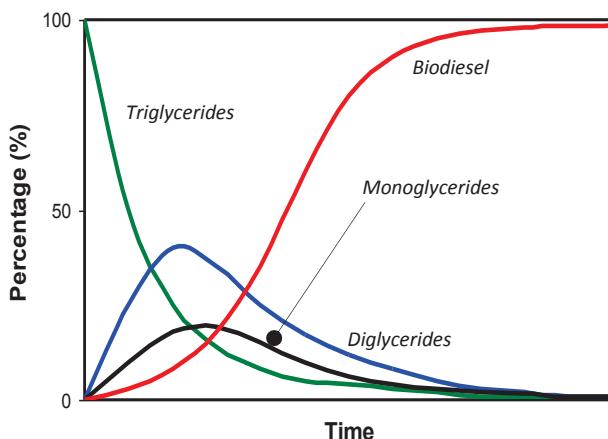


Figure 5. Illustration of conversion rates in transesterification of triglycerides with methanol.

Since transesterification is a reversible reaction, if stoichiometric reactants are used, i.e., 3 mol of methanol reacting with 1 mol of triglyceride, the reaction will reach equilibrium after a certain reaction time. At that time the reaction mixture will contain esters, mono-glycerides, and di-glycerides, as well as the reactants of triglycerides and methanol. Since biodiesel producers are interested in producing as much biodiesel as possible by converting all of the oil or fat in the system, they generally add twice as much methanol as stoichiometrically required (i.e., 100% excess, or a methanol to oil molar ratio of 6:1). The additional methanol drives the reaction towards the biodiesel, resulting in a completion of triglyceride conversion to biodiesel, according to Le Chatelier's principle.

In this laboratory, we will be learning the concept of chemical equilibrium by experimenting with converting soybean oil, a vegetable oil composed of triglycerides, into biodiesel through a two-step process.

Pre-Lab Questions:

1. Why do some reactions reverse themselves, while others do not?
2. What are some things you can do to force a reaction in one direction?

3. What do biodiesel producers do to push the transesterification reaction in the direction of biodiesel production?

Safety Note: Because of the potentially dangerous chemicals used in this lab, everyone must wear safety glasses or goggles while working in the laboratory. Lab coats or aprons should be worn when pouring or mixing chemicals. If a fire occurs, leave the building immediately and call 911. Do not try to fight it!

Laboratory Procedure

Procedure for making a small batch of biodiesel in two stages

Stage 1 Transesterification with stoichiometric reactants

1. Weigh out 1 g of potassium hydroxide into a 125 mL Erlenmeyer flask. Into this same flask add 20 g of methanol to an accuracy of 0.01 g (this amount is equivalent to 6:1, or twice the stoichiometric molar ratio of methanol to oil). Add a stir bar, cover with aluminum foil, and place on a magnetic stirrer. Mix until the KOH is completely dissolved. Set this aside.
2. Weigh an empty 250 mL Erlenmeyer flask and record the weight (to an accuracy of 0.01 g) in Table 1 (this will be used later to calculate your biodiesel yield). Weigh out about 100 g of soybean oil to an accuracy of 0.01 g into this same flask and record in Table 1. Add a stir bar, put on a hot plate, and start to heat the oil to around 60 °C.
3. Once 60 °C is reached, add half (or approximately 10 g) of the alcohol/catalyst mixture to the flask (this will give you close to a 3:1 or stoichiometric molar ratio of methanol to oil) and cover with a watch glass or aluminum foil to keep the alcohol vapors from escaping. Stir this mixture at a moderate level at 60 °C to react for 60 min.
4. Stop heating and stirring. Carefully transfer the mixture to a separatory funnel and allow it to cool down and separate for 20 min.⁵
5. Weigh a 125-mL flask (to an accuracy of 0.01 g) and record the weight. Remove the glycerol (lower) layer carefully from the bottom of the funnel into this pre-weighed flask. The upper layer is the biodiesel phase, and the separated lower layer is the crude glycerol with some catalyst in it.
6. Weigh the flask with separated glycerol (to an accuracy of 0.01 g) and record the net weight into Table 1.

⁵ **Note:** If there is no phase separation after 5 to 10 min, it can be forced by adding water to it. Return the mixture to the 250 mL Erlenmeyer flask, while stirring, add 15 mL of water and continue to stir for about 10 seconds. Then, return the mixture to the separatory funnel. This action will concentrate the polar molecules of water, methanol and glycerol and allow them to settle along with a good portion of the soap (the undesired byproduct).

7. Save the biodiesel phase for later use.

The first step of the reaction is now finished. Based on the crude glycerol weight, calculate the estimated biodiesel yield, and compare this with the theoretical yield, assuming 100% soybean oil conversion⁶. Discuss:

- How much soybean oil has converted to biodiesel? Has all the soybean oil been converted? Is the reaction complete?
- If not, could the reaction be complete if we extended the reaction time by another 2 hours? Why or why not?
- According to Le Chatelier's principle and the nature of transesterification, what is/are the possible way(s) you could improve the conversion of soybean oil (or to help the reaction move forwards to the right)?

Stage 2 Transesterification with additional methanol (to complete the reaction)

1. Transfer the saved biodiesel from the previous step into the original reaction flask. Add a stir bar, put on a hot plate, and start to heat the solution again to around 60 °C.
2. Once 60 °C is reached, add the remaining alcohol/catalyst mixture to the flask and cover with a watch glass or aluminum foil to keep the alcohol vapors from escaping. Stir this mixture at a moderate level for 60 min at 60 °C to react.
3. Stop heating and stirring. Carefully transfer the mixture to a separatory funnel and allow it to cool down and separate for 20 min.⁷
4. Remove the glycerol (lower) layer carefully from the bottom of the funnel into the same flask containing crude glycerol from the previous stage.
5. Weigh the flask with the separated glycerol and record the net weight (to an accuracy of 0.01 g) into Table 2.

⁶ Hint: the theoretical molar yield of biodiesel is the same as the theoretical yield of glycerol based on the stoichiometric ratios in the transesterification (Fig. 2). For every mol of soybean oil (MW = 877 g/mol), there is 1 mol of glycerol formed (glycerol MW = 92.1 g/mol). For 100 g soybean oil used for this laboratory, it is equivalent to $100 \text{ g} / 877 \text{ g/mol} = 0.114 \text{ mol}$; the theoretical yield of glycerol will be $0.114 \text{ mol} \times 92.1 \text{ g/mol} = 10.5 \text{ g}$.

⁷ Note: If there is no phase separation after 5 to 10 min, it can be forced by adding water to it. Return the mixture to the 250 mL Erlenmeyer flask, while stirring, add 15 mL of water and continue to stir for about 10 seconds. Then, return the mixture to the separatory funnel. This action will concentrate the polar molecules of water, methanol and glycerol and allow them to settle along with a good portion of the soap (the undesired byproduct).

Based on the crude glycerol weight, again calculate the estimated biodiesel yield, and compare this with the theoretical yield, assuming 100% soybean oil conversion⁸. Discuss:

- How much soybean oil has converted to biodiesel? Has all the soybean oil been converted? Is the reaction complete?

Laboratory Observations

Color change of the reaction mixture from start to finish point:

Glycerol formation and separation:

⁸ Hint: the theoretical molar yield of biodiesel is the same as the theoretical yield of glycerol based on the stoichiometric ratios in the transesterification (Fig. 2). For every mol of soybean oil (MW = 877 g/mol), there is 1 mol of glycerol formed (glycerol MW = 92.1 g/mol). For 100 g soybean oil used for this laboratory, it is equivalent to $100 \text{ g} / 877 \text{ g/mol} = 0.114 \text{ mol}$; the theoretical yield of glycerol will be $0.114 \text{ mol} \times 92.1 \text{ g/mol} = 10.5 \text{ g}$.

Biodiesel Fundamentals for High School Chemistry Classes



Data collection and processing

Table 1

Category	Item	Variable	Quantity (g)
Soybean oil	Flask weight	W_{ini}	
	Flask + sample	W_{end}	
	Net sample size	W_{soy}	
Crude glycerol	Flask weight	$W_{ini,1}$	
	Flask + sample	$W_{end,1}$	
	Net sample size	$W_{gly,1}$	

Calculate the soybean oil (MW = 877 g/mol) added in moles:

$$m_{soy} = W_{soy} / 877 \text{ (mol)}$$

This is the equivalent molar amount of theoretical glycerol yield, or

$$m_{soy} = m_{gly,theo}$$

Actual glycerol (MW = 92.1 g/mol) molar yield in this stage:

$$m_{gly,actual,1} = W_{gly,1} / 92.1 \text{ (mol)}$$

Therefore, the degree of overall reaction (or overall conversion of soybean oil) is:

$$R_1(\%) = m_{gly,actual,1} / m_{gly,theo} \times 100$$

Table 2

Category	Item	Variable	Quantity (g)
Crude glycerol	Flask + previous sample	$W_{ini,2}$	
	Flask + new sample	$W_{end,2}$	
	Net total sample size	$W_{gly,2}$	

Actual glycerol (MW = 92.1 g/mol) molar yield in this stage:

$$m_{gly,actual,2} = W_{gly,2} / 92.1 \text{ (mol)}$$

Therefore, the degree of overall reaction (or overall conversion of soybean oil) is:

$$R_2 (\%) = m_{gly,actual,2} / m_{gly,theo} \times 100$$