3.4.1: Environment- Synthesis of Biodiesel Fuel

Biological oils are different from petroleum oils ("regular" diesel fuel) in molecular structure and properties.

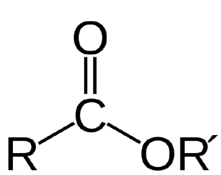
Some cities are converting their bus lines to biodiesel

Common petroleum diesel fuel is a mixture of simple hydrocarbons, with the average chemical formula $C_{12}H_{23}$ (shown below), but components may range approximately from $C_{10}H_{20}$ (dodecane) to $C_{15}H_{28}$(pentadecane).[1] By contrast, biological oils are "triglycerides" (classified as "esters") like the glyceryl trilinoleate shown below:

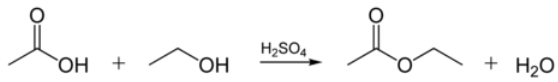
$C_{12}H_{23}$, dodecane	A triglyceride: glyceryl trilinoleate

Because of their large size and consequent large intermolecular attractions, the viscosity of biological oils is generally too high for use in conventional diesel engines. Biological oils also burn a little less readily, and with a sootier flame than petroleum diesel. Biological oils can be used in conventional diesel engines if they are preheated to reduce their viscosity, but this requires an auxiliary electrical heater until the engine warms up. For these resons, bilogical oils require processing for use as biodiesel.

A biological oil is an ester, which is a type of organic compound having the atom linkage shown below.

 The ester linkage. R and R' represent chains of carbon and hydrogen atoms. R = $-CH_3$ and R' = $-C_{18}H_{35}O_2$ for the methyl stearate in Example 1	glycerol

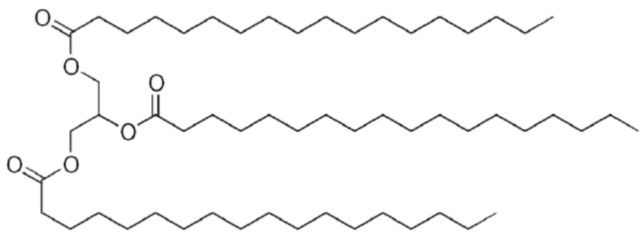
The ester linkage in biological oils is created when a glycerol molecule reacts with organic acids. The glycerol molecule has a chain of 3 carbon atoms, each with an -OH (alcohol) group on it. The figure below shows how an organic alcohol reacts with a organic acid. Organic chemists abbreviate molecular structures--the "zig-zag" lines in the figure represent carbon chains with a C atom at each "zig" or "zag". Each carbon has 4 bonds, and if fewer than 4 are shown, it's assumed that they go to H atoms. So the alcohol is C_2H_5OH (ethanol), and the acid is acetic acid (or ethanoic acid, CH_3COOH) in the Figure:



Equation for ester formation is shown in terms of molecular structures. Acetic acid plus ethanol gives ethyl acetate and water.

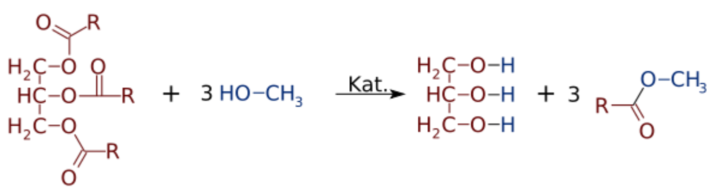
Organic Acid + Alcohol → (with sulfuric acid catalyst) an ***ester*** and water

Since glycerol has 3 -OH groups, 3 long chain organic "fatty acids" attach to make the bulky "triglyceride".



Stearin, or glyceryl tristearate

But just as easily as esters can be made from alcohols and acids, they can switch alcohols or acids. In the presence of a strong base catalyst, like NaOH, a triglyceride can react with 3 small alcohol molecules, like methanol (CH_3OH), which replace the glycerol "backbone", making 3 separate esters of lower molecular weight



Quite often a mixture of two or more products is formed. For example, when a vegetable oil reacts with methanol, only one or two of the acids may be displaced from the glycerine, producing only 1 or 2 FAMEs.

$C_3H_5(C_{18}H_{35}O_2)_3 + NaOH + 2\ CH_3OH \rightarrow C_3H_5(C_{18}H_{35}O_2)_2(OH) + 2\ C_{17}H_{35}COOCH_3$

$C_3H_5(C_{18}H_{35}O_2)_3 + NaOH + 1\ CH_3OH \rightarrow C_3H_5(C_{18}H_{35}O_2)(OH)_2 + 1\ C_{17}H_{35}COOCH_3$

$C_3H_5(C_{18}H_{35}O_2)_3 + NaOH + 3\ CH_3OH \rightarrow C_3H_5(OH)_3 + 3\ C_{17}H_{35}COOCH_3$

Usually, a large excess of methanol and sodium hydroxide are added, so that the reaction produces the maximum amount of FAME.

But in the case of a transesterification, even though none of the reactants is completely consumed, no further increase in the amounts of the products occurs. We say that such a reaction does not *go to completion*. When a mixture of products is produced or a reaction does not go to completion, the effectiveness of the reaction is usually evaluated in terms of **percent yield** of the desired product. A **theoretical yield** is calculated by assuming that all the limiting reagent is converted to product. The experimentally determined mass of product is then compared to the theoretical yield and expressed as a percentage:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent}$$

EXAMPLE 1 When 100.0 g $C_3H_5(C_{18}H_{35}O_2)_3$ gas and 15.0 g CH_3OH are mixed at 55°C with NaOH catalyst, they react to form 90.96 g $C_{17}H_{35}COOCH_3$ methyl stearate biodiesel. Calculate the percent yield.

Solution

We must calculate the theoretical yield of NH_3, and to do this, we must first discover whether N_2 or H_2 is the limiting reagent. For the balanced equation

$C_3H_5(C_{18}H_{35}O_2)_3$ + NaOH + 3 CH_3OH → $C_3H_5(OH)_3$ + 3 $C_{17}H_{35}COOCH_3$

stearin + sodium hydroxide + 3 CH_3OH → glycerol + 3 methyl stearate

The stoichiometric ratio of the reactants is

$S\left(\frac{\text{stearin}}{\text{CH}_3\text{OH}}\right) = \frac{1 \text{ mol stearin}}{3 \text{ mol CH}_3\text{OH}}$ Now, the initial amounts of the two reagents are and

$$n_{\text{stearin}}(\text{initial}) = 100.0 \text{ g stearin} \times \frac{1 \text{ mol stearin}}{891.5 \text{ stearin}} = 0.1122 \text{ mol stearin} \tag{3.4.1.1}$$

$$\tag{3.4.1.2}$$

$$n_{\text{CH}_3\text{OH}}(\text{initial}) = 15.0 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} = 0.4682 \text{ mol CH}_3\text{OH} \tag{3.4.1.3}$$

The ratio of initial amounts is thus $\frac{n_{\text{stearin}}(\text{initial})}{n_{\text{CH}_3\text{OH}}(\text{initial}} = \frac{0.1122 \text{ mol stearin}}{0.4682 \text{ mol CH}_3\text{OH}} = \frac{0.240 \text{ mol stearin}}{1 \text{ mol CH}_3\text{OH}}$ Since this ratio is less than $S\left(\frac{\text{stearin}}{\text{CH}_3\text{OH}}\right) = 0.33$, there is an excess of CH_3OH. Stearin is the limiting reagent. Accordingly we must use 0.1122 mol stearin and 0.3366 mol CH_3OH (rather than 0.4682 mol CH_3OH) to calculate the theoretical yield of $C_{17}H_{35}COOCH_3$ (methyl stearate). We then have $n_{\text{methyl stearate}}(\text{theoretical}) = 0.1122 \text{ mol stearin} \times \frac{3 \text{ mol methyl stearate}}{1 \text{ mol stearin}} = 0.3365 \text{ mol methyl stearate}$ so that $\text{m}_{\text{methyl stearate}}(\text{theoretical}) = 0.3365 \text{ mol methyl stearate} \times \frac{298.51 \text{ g methyl stearate}}{1 \text{ mol methyl stearate}} = 100.5 \text{ g methyl stearate}$ We can organize these calculations in a table:

	$C_3H_5(C_{18}H_{35}O_2)_3(s)$	+ 3 CH_3OH (l)	→ 1 $C_3H_5(OH)_3$ (l)	+ 3 $C_{18}H_{35}O_2)_3CH_3(s)$
m, g	100.0 g	15.00 g		90.96 g
M, g/mol	891.5	32.04	298.5	92.1
n present, mol	0.1122 mol	0.4682 mol		
n actual, mol	0.1122	0.3366	0.1122	0.3366
m actual, mass	100.0	10.78	10.33	100.47

The percent yield is then $\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent} = \frac{90.96 \text{ g}}{100.5 \text{ g}} \times 100 \text{ percent} = 90.55 \text{ percent}$

Transesterification is a classic example of a reaction which does not go to completion.

References

1. en.Wikipedia.org/wiki/Diesel_fuel