THE DEVELOPMENT OF KINETIC MODEL FOR BIODIESEL PRODUCTION USING IMMOBILIZED ENZYME

Introduction

Fossil fuel or petroleum has become the major source of combustible energy and had been used worldwide to power up industries, transportations, domestic uses as well as many other purposes. However, petroleum is not renewable and years of over usage, we are now facing with energetic crises due to depletion of its resources. Besides that, the increased population as well as environmental pollution had increases our concern to find an alternative to our conventional fuel towards something renewable, environmental-friendly and able to sustain global demand.

Among the many possible sources, biodiesel derived from plant oil (PO) attracts attention as a promising one for substitution or blending with conventional diesel-based fuels. If pure or blend biodiesel is used as fuel, the net production of carbon dioxide can be suppressed, thus helps to decrease harmful carbon based fume into atmosphere which will lead to global warming. The plant oil is renewable, nontoxic, and widely available from a variety of sources and has low sulfur contents close to zero. Oil crops such as palm, soybean, sunflower, peanut, and olive oils are used as an alternative fuel for diesel engines.

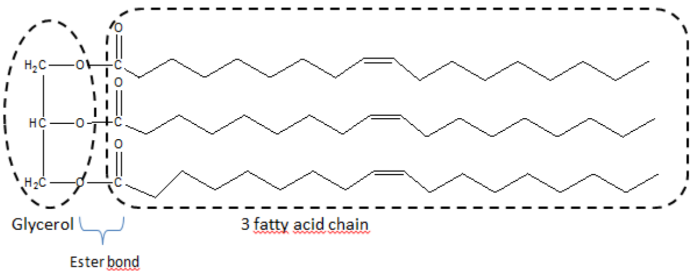

Figure 1: Triglyceride

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The main components inside plant oil is a substance called triglyceride (TG) which consist of 1 molecule of glycerol attached to 3 molecule of fatty acid chain (Fig. 1). These ester compound doesn't mix with water but soluble in organic solvents such as hexane or petroleum ether. The length and the nature of fatty acid chain vary according to its sources. For example, in coconut oil, the major fatty acid chain have 12 to 14 carbon atoms in a chain and all are link to each other in a single bonding, hence, it is called saturated fatty acid. Soybean oil on the other hand, mainly has 18 carbon atoms linked in the fatty acid chain and some atoms were linked in a special bonding called double bonds. Hence it is called unsaturated fatty acid. Saturated fatty acid can easily turn into solid texture compared to unsaturated fatty acid. Due to this feature the usage of plant oil can be varied according to its thermal properties. Plant oil is slightly thicker if compared to diesel fuel and also ignites at higher temperature. In order to make it easier to ignite, a chemical transformation process called transesterification is performed to plant oil where TG is transformed into fatty acid methyl esters or FAME. FAME has lower boiling point and has the fluidity characteristic similar to petroleum diesel. This substance is what is meant by biodiesel.

The objective of transesterification is to change TG into FAME to lower its ignition temperature. The bonds between glycerol and fatty acid chain is chemically cut and the free fatty acid (FFA) will the form a new bond with another chemical compound which is similar to glycerol but smaller in size called methanol. Bonding of FFA and methanol will create FAME. This chemical reaction requires heat, physical agitation, and catalyst to accelerate and control the equilibrium, so that in the end more FAME is produced.

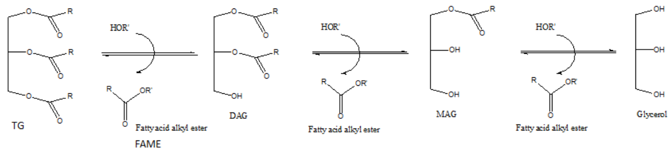

Figure 2: Reaction scheme of transesterification

The overall process is a sequence of three consecutive and reversible reactions (Fig. 2). In order to speed up the process, we need a special compound called catalyst. It can be chemical compound, either acid or base. Or if we wish for something 'greener', we can utilize biocatalyst or enzyme. The advantage of using enzyme is that the reaction requires low heat and energy, produces pure products and easy separation, and more environmental friendly compared to acid or base catalyst. Specific enzyme used for transesterification is called lipase enzyme. It can be cultivated endlessly from bacteria or microorganism. Enzyme can be added into reaction mixture as it is (free enzyme), or, it can also be supported on a carrier (immobilized enzyme).

Kinetic analysis - The recipe to success

Chemists are just like chefs. Performing a chemical reaction requires knowledge and expertise to identify the optimal conditions so that the highest yield can be obtained. Kinetic studies are just like recipe used by chefs to prepare an exquisite delicacy. Only a small number of kinetic studies on the transesterification of oils by immobilized lipases have been found in the literature.

In Aarhus University, led by Lipid Lab, a scientific research is conducted to analyze the kinetic mechanism on lipase catalytic reaction.

Kinetic analysis is a complex study where a series of variables needs to be calculated to obtain an optimum condition for the reaction. Optimization of such process is, however, not an easy task. First of all, the reaction is reversible, and increasing concentrations of alcohol (methanol) are required to shift the direction of the reaction preferably towards high yield. However, methanol is known to be poisonous to enzyme where high concentration of this substance will kill them. A good knowledge of the reaction kinetics and inhibition patterns is necessary to reach a high conversion degree preserving at the same time the enzymatic activity.

Determination of the necessary kinetic constants is not an easy task when working with complex reaction. For example, the complete set of substrates (initial ingredients) and products in oil–biodiesel mixtures includes tri-, di and monoglycerides (TG, DG, and MG), free fatty acids (FA), water (W), glycerol (G), alcohol (C) and biodiesel (B). The situation is complicated by involvement of several reactants in phase transitions and inhibition of the enzyme. Elements that need to be measure in kinetic analysis are the speed of reaction (reaction velocity), the rate constants and rate coefficient. More than 20 rate constants need to be evaluate and it is almost impossible to determine them all in one experimental set up. So, the Lipid Lab group took a clever step of disassemble the main complex reaction into different blocks of individual reaction and evaluate the rate constant independently (Fig. 3) This strategy not only minimizes the number compounds to be evaluated, but also helps to make the velocity equations less complex and hence make the analysis more reliable.

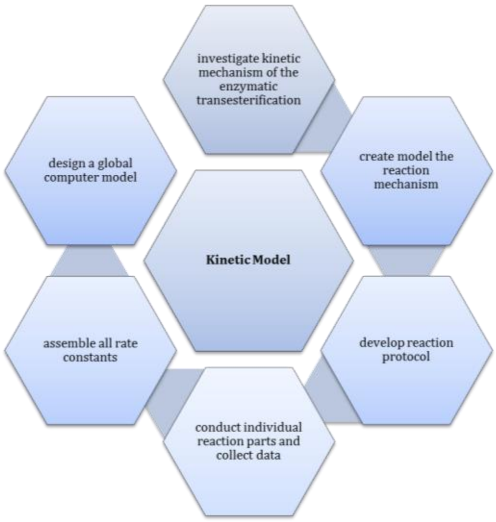

Figure 3: Development of kinetic model for production of biodiesel.

Separate assessment also gives the opportunity for researchers to evaluate how water affects the kinetic behavior at the initial part as well the end of the reaction (or equilibrium state). The opposite reaction of forming ester bonds is the dissociation of the bond by the presents of water, namely as hydrolysis process. High concentration of water will cause failure for biodiesel formation but without water enzyme will not be activate.

Once all necessary constants were derived, the result of all individual analysis will be reconstructed back into global kinetic model which can be utilize to as mathematical mean to optimize the reaction condition. This model can help scientist or manufacturers give an early assumption, for example to estimate how much enzyme needed to be use in a reaction and what possible yield can be obtained at the end. The model also gives beneficial information to the manufacturer on the type of raw material that can be used for a certain enzyme. So far, there are two successful model had been constructed for lipase enzyme derived from Candida antartica Lipase B (CALB) and Thermomyces lanuginosis Lipase (TL)

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