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Kinetic Processes Simulation for Production of the Biodiesel with Using as Enzyme

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Abstract

The esters components were produced by transesterification of the plant oil or for animal fat with methanol in the presence of a catalyst such as **(lapis)** enzyme. The rate of transesterification in a batch reactor increased with temperature increasing the temperature. Higher temperatures did not reduce the time to reach maximal conversion for the ester production. The conversion process of the triglycerides (TG), diglycerides (DG) and monoglycerides (MG) was observed into concentration of **(Es)** with time. The effect of Al concentration increasing is studied in this paper. The effect of Al concentration increasing that leads to appearance of behaviors on the results which agree with other researches and which matching with the predicted behaviors that are appeared on the results which agree with other researches and which matching with the predicted behaviors.

Keywords: Enzymatic processes, Biodiesel, Kinetic, Catalysis.

Introduction

Biodiesel is an attractive alternative to petroleum diesel. Production of biodiesel is easily done and requires low energy inputs [1]. While it can be made from animal fat, the main fuel stock is vegetable oil, which can be obtained from an amazing variety of plants. Biodiesel is more environmental friendly as it produces from natural resources and from the waste [2,3]. Basically, biodiesel are vegetable oils and animal fats which undergo a process known as transesterification to produce glycerol and fatty acid alkyl esters [2].

This processes is included the effect of the two types of Catalysts, homogenous and heterogeneous. Catalyst has a positive effect on the liquefaction process and can increase the yield of liquid product, as well as improve the quality of liquid product. With a catalyst, more bio-oil and less gas can be obtained than that without using a catalyst [4].

Catalysts are important in hydrothermal liquefaction processes and are used for improving gasification efficiency, suppress tar and char formation.

Homogeneous catalysts in forms of alkali salts have been frequently used, whereas heterogeneous catalysts such as various form for catalysts has been less frequently utilized in hydrothermal liquefaction. On the other hand, heterogeneous catalysts are widely used in low-temperature water gasification of biomass. In chemistry and biology, catalysis is the acceleration (increase in rate) of a chemical reaction by means of a substance [4, 5].

Biodiesel Production Process

Biodiesel is produced from vegetable oils or animal fats and an alcohol, through a transesterification reaction. The behavior of chemical reaction that converts the ester (vegetable oil or animal fat) into a mixture of esters of the fatty acids that makes up the oil (or fat) [6,7]. Biodiesel is obtained from the purification of the mixture of fatty acid methyl esters (FAME). A catalyst is used to accelerate the reaction. According to the catalyst used, transesterification can be basic, acidic or enzymatic, the former being the most frequently used, as indicated in references used[] , the reaction product would be a mixture of ethyl esters. In both cases, glycerin will be the co-product of the reaction[6].

Theory

Biodiesel is produced from fat. It can be resulted from vegetable oil or from the animal fat type. Waste vegetable oil can be used to make quality biodiesel. Fats are converted to biodiesel through a chemical reaction involving alcohol and a catalyst. The principal ways of making biodiesel are by transesterification of triglycerides and esterification of free fatty acids. The chemical kinetics of transesterification, the most common means of producing biodiesel, remains controversial. Most efforts in the literature have focused on finding the best fit of empirical data to simple models of reaction order. Some of these results are contradictory. The rate of reaction is then dependent solely on the concentration of triglyceride. The modeling of biodiesel production is solved by using matlab program with numerical method is defined as (ode45) Runge- Kutta for fourth order.

Methyl esters derived from vegetable oil (biodiesel) have good potential as an alternative diesel fuel. The energy content., viscosity, and phase changes of biodiesel are similar to those of petroleum-based diesel fuel[8]. Biodiesel is produced by transesterification of large, branched triglycerides (TG) into smaller, straight-chain molecules of methyl esters, using an alkali or acid as catalyst. There are three stepwise reactions with intermediate formation of diglycerides (DG) and monoglycerides (MG) resulting in the production of *(3 mol*) of methyl esters (ME) and 1 mol of glycerol (GL) as follows[6-9]:

$$TG + 3ROH \xrightarrow{Catalyst} 3R'CO_2\text{-}R + GL \qquad [1]$$

This process can be modeling by using matlab program

$$TG + ROH \underset{k_4}{\overset{k_1}{\rightleftharpoons}} DG + R'CO_2R \qquad [2]$$

$$DG + ROH \underset{k_5}{\overset{k_2}{\rightleftharpoons}} MG + R'CO_2R \qquad [3]$$

$$MG + ROH \underset{k_6}{\overset{k_3}{\rightleftharpoons}} GL + R'CO_2R \qquad [4]$$

The enzyme as Catalyst

Enzyme catalysts have also been considered for biodiesel production. Enzyme catalysts are often considered in order to reduce the environmental impact of chemical processes because high conversions are possible at relatively benign operating conditions. The type of enzyme catalysts used to investigate biodiesel production is lipases types. Another advantage of enzymes is that the saponification side reaction does not occur. The catalysts used for the transesterification of triglycerides may be classified as basic, acid or enzymatic [6, 10]. Basic catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates and their corresponding alcoxides (for instance, sodium methoxide or ethoxide). There are many references on basic catalysts in the scientific literature [11].

Enzymatic Reaction Mechanism

The function of biological for lipases enzyme is to catalyst the breakdown of lipids as part of the metabolism of living cells which generally exist in a water rich environment. This leads to the formation of carboxylic acids and short chain alcohols [12]. Lipases have been designed by nature to catalyse the cleavage of ester bonds by means of a hydrolysis reaction in water rich environments. However the reverse esterification reaction is possible depending on the reaction environment. The active site targets carboxyl groups which are a characteristic functional group on lipids such monoglycerides (MG), diglycerides (DG), triglycerides (TG), FFAs and esters, including FAME. The structural conformation of the enzyme and lipid will determine if the carboxyl group is able to reach the active site. Lipases can catalyse esterification, transesterification and hydrolysis involving MGs, DG, TGs, FAME. Environmentally Benign Biodiesel Production by Heterogeneous Catalysis and FFAs that depending on the type of lipase and the reaction medium. Heterogeneous catalysts that have been considered for biodiesel production include enzymes [13], titanium silicates [14], and compounds from alkaline earth metals [16], anion exchange resins [15] and guanidines in organic material [14].It is most common to use homogeneous alkali catalysts for the transesterification reaction. This yields high reaction rates at low operational costs (ambient temperatures and pressures). However, the homogeneous catalyst can be difficult to recover, they cause damage to the column due to corrosive properties and waste treatment and contamination can be a challenge post-reaction [17]. The catalysts are usually present at concentrations of approximately 1 percent, and the most common catalysts are NaOH, KOH or sodium methoxide, with sodium hydroxide being the cheapest and most popular alternative. Thus the NaOH is also the catalyst with the highest costs associated with waste disposal, cleaning, damage to the column and also the one which has the most negative impact on the environment [10]. Analysis of process: The samples were analyzed for TG, DG, MG, total methyl esters, and glycerol content by gel permeation Chromatography.

Water effect

The concentration of water leads to increase the hydrolysis side reaction is favored. It should be possible to convert the FFAs to FAME using enzyme as catalyst, thus increasing the TG conversion; however the aim of one stage is to maximum value of the TG conversion. Like as high TG conversions are achieved when the limit ratio of water in the characterize range are added to the reaction mixture [16]. The addition and subsequent removal of water will increase the costs and it is preferable to minimum value of the amount of water added. On this basis the optimum water additions for limit value [13].

The values for the rate constants and the activation energies of the reactions, in the form of the Arrhenius Equation which is displayed below as equations (5) [18,19].

$$k_i = A_i \cdot \exp\left(\frac{Ea_i}{RT}\right) \qquad [5]$$

The mathematical model

The kinetic mechanisms of production biodiesel by enzyme are described by the coupled system that express of the changing of the concentrations of reactors. These dynamics of biodiesel production is given by [20]:

$$\frac{d[T]}{dt} = -(L_{mT}[W] + L_{eT}[Al][T][X] \ (6)$$

$$\frac{d[D]}{dt} = ((L_{mT}[W] + L_{eT}[Al])[T] - (L_{mD}[W] + L_{eD}[Al])[D])[X](7)$$

$$\frac{d[M]}{dt} = ((L_{mD}[W] + L_{eD}[Al])[D] - (L_{mM}[W] + L_{eM}[Al])[D])[M])[X](8)$$

$$\frac{d[G]}{dt} = (L_{mM}[W] + L_{eM}[Al])[X](9)$$

$$\frac{d[F]}{dt} = -\frac{d[W]}{dt} = ((L_{mT}[T] + L_{mD}[D] + L_{mM}[M])[W] - L_{eEs}[F][Al])[X](10)\ m)$$

$$\frac{d[Es]}{dt} = -\frac{d[Al]}{dt} = (L_{eT}[T] + L_{eD}[D] + L_{eM}[M] + L_{eEs}[F])[Al][X](11)$$

Where [X] is given by:

$$[X] = \frac{Etotal}{(1 + K_{mT}[T] + K_{mD}[D] + K_{nM}[M] + K_{mF}[F] + (\frac{Al}{K_I})} \qquad (12)$$

Transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, sunflower, and safflower. Common catalysts for transesterification are NaOH, KOH, or sodium methoxide[15]. The sodium methoxide causes formation of several by-products, mainly sodium salts, which have to be treated as waste. In addition, high-quality oil is required with this catalyst. KoH catalyst has an advantage in that, at the end of the reaction, the reaction mixture can be neutralized with phosphoricacid resulting in potassium phosphate, which can be used as fertilizer[6]. The kinetics of transesterification will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions[10]. Among several kinetic studies published on transesterifieation of simple esters, only a few were concerned with the transesterifieation of Vegetable [6].

Results and discussion

The results of this paper are introduced the summarizing of the effects and concentrations of reactions at initial values. The parameters of theoretical model are given by table (1).

Table (1): Parameters of theoretical model(hydrolysis rate constants and) [6].

Parameters symbols	**Values** $((mol^{-1}.\min^{-1}))$
(LmT) hydrolysis rate constant	0.0130
(LmD) hydrolysis rate constant	0.447
(LmM) hydrolysis rate constant	78.6
LeEs -esterification rate constant	48.4
LeT- transesterification	0.00430
LeD- transesterification	25.5
LeM- transesterification	18.5 16.1
KmT- transesterification	0.00770
KmD- the inhibition constant	0.00290
KmM- the inhibition constant	3.92
KmF- the inhibition constant	0.00410
KI- the inhibition constant	764

The results that described the concetations of (TG,DG,Es,Al,GL and W) that are shown in figure(1). Figure(2) shows the effect of increasing of Al on the Es concetration in the reactions of kinetics with enzymatic processes (enzyme as catalyst) and figure (3) represents the affeting of increasing of Al on the Es concetraction.

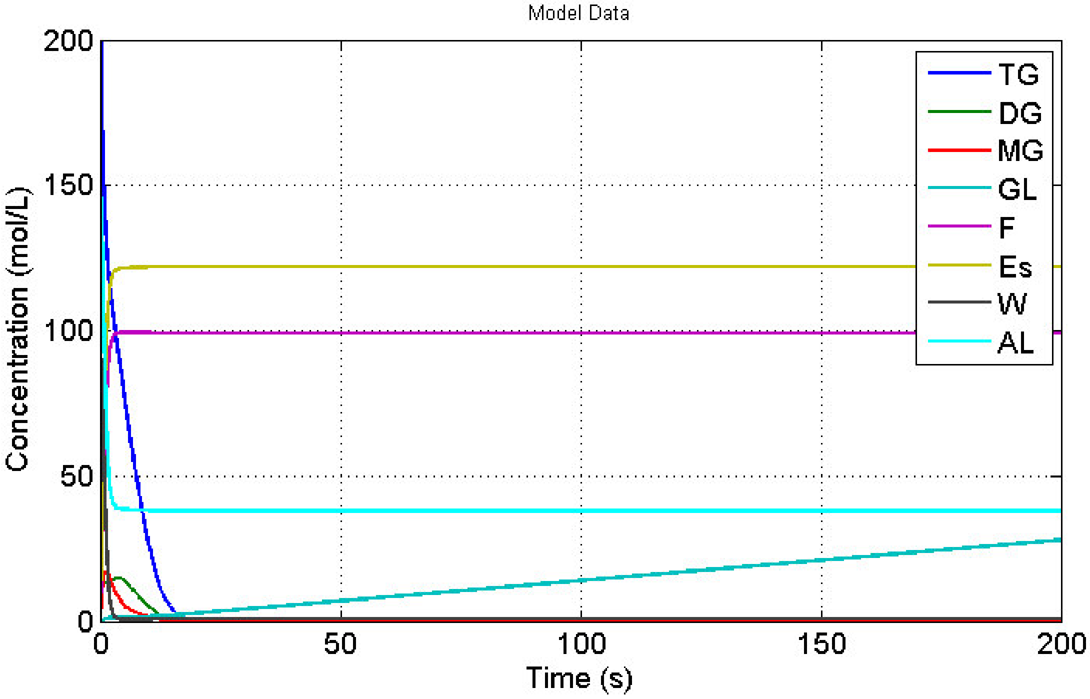

Figure (1): The concentrations of (TG, DG, Es, Al, GL and W).

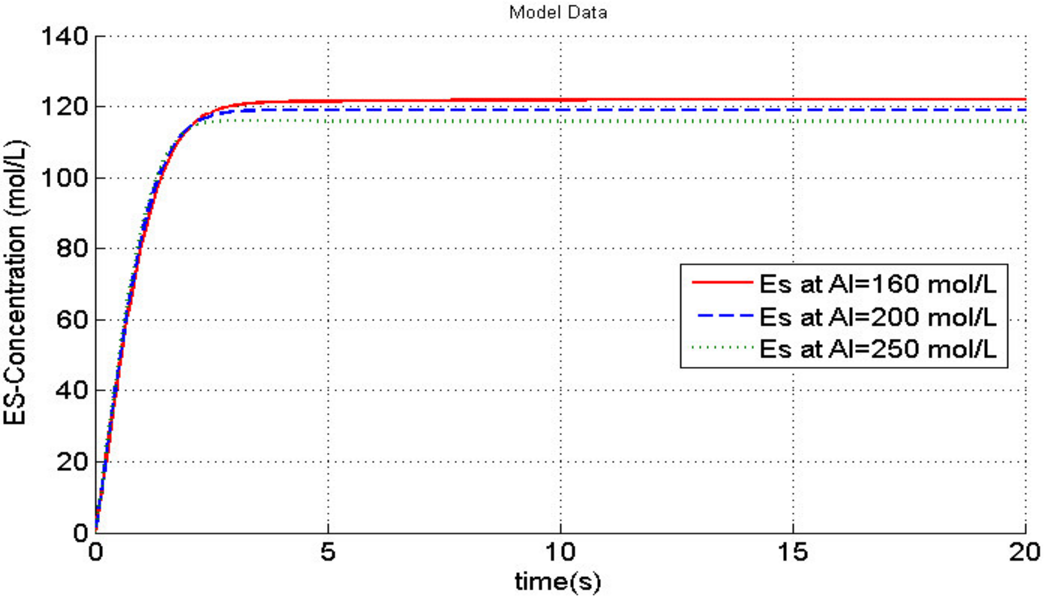

Figure (2) shows the effect of increasing of Al on the Es concentration in the reactions of kinetics with enzymatic processes (enzyme as catalyst).

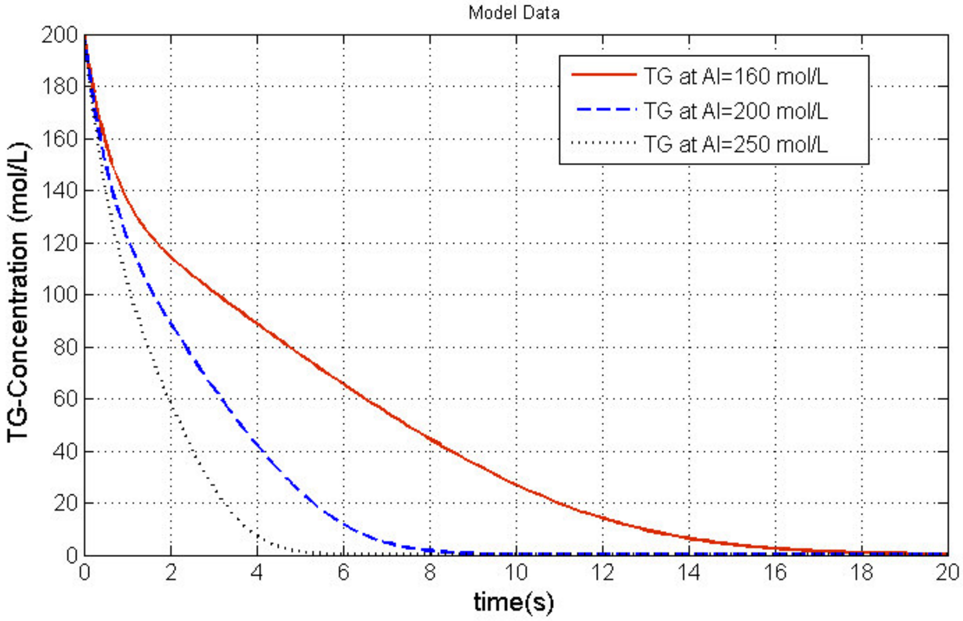

Figure (3): represents the affecting of increasing of Al on the Es concentration.

Conclusions

We note that the concentrations of reactions are varied at the parameters in table (1). These results summarize the effect of **Al** concentration increasing. These behaviors that are appeared on the results which agree with other researches and which matching with the predicted behaviors.

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