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Determination of kinetic parameters for the reactions involved in biodiesel production via optimization approach

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Abstract: Biodiesel is one the most promising alternative fuel now a days, commonly produced by the transesterification of vegetable oils and fats. Transesterification reaction involves three steps producing biodiesel in each step by the reaction of Tri, di and mono glyceride with alcohol. In current study general reaction kinetic model has been developed for all the reactions involved in Biodiesel production using MALTAB to obtain optimum kinetic data which will be compared with the experimental data for validation. The optimization of kinetic parameters involved in the synthesis of biodiesel is performed by using MATLAB optimization toolbox. The results show that the model sounds good agreement with the experimental data with a minimum error of **±5**.

Key words: Biodiesel; Transesterification; Rate Constant; Optimization; MATLAB

1. Introduction

Fossil fuels are organic or covalently bonded carbon containing substances in the form of solid, liquid or gas that have been produced by plants and animal remains which undergone chemical and physical transformation over hundreds of years. Fossil fuels have become the world's primary source of energy. It is estimated about 85% of energy production was contributed by fossil fuel in 2010 (Dewallef, 2014). Fossil fuels are considered as non-renewable energy as the process of production of fossil fuel takes over geological time periods, alternative sources of energy have to be developed in order to curb the depletion of fossil fuels. Alternative source of energy simply means fuels from renewable sources such biomass. Biofuels are one of several alternative renewable energy source that being developed nowadays.

Bio -fuels mainly derived from bio-mass which consist of organic waste such as agricultural waste, biological waste and forest waste (Ju et al., 2009). There are different types of biomass which includes empty fruit branches, sugarcane bagasse, sawdust, rice husk, manure, grass crops, forest residues and municipal solid waste. These types of biomass are used to derive different types of product including natural palm oil fiber strand, geotextiles, biomass wood pellet, briquette from straw and hay, cork flooring and compost from municipal solid waste for agriculture.

At present, about 80% of all primary energy in this world is derived from fossil fuel with oil accounting for 32.8%, coal for 27.2% and natural gas for 20.9% (IEA, 2011). Alternative sources of energy only contribute approximately 20 % of world energy source. The biofuels could not fully replace current fossil fuels as biofuels are combined with fossil fuels to be used in current technologies. There is need to carry out more studies to optimize the efficiency of biofuels in current technologies.

Biodiesel as a renewable alternative fuel has become the most attractive fuel these days due its environmental benefits commonly produced from vegetable oil and fats with the addition of alcohol (commonly methanol) and the use of catalyst forming fatty acid alkyl esters by a process known as transesterification or alcoholysis (Leung et al., 2010). Feedstock includes rapeseeds, sunflower seeds, soy seeds, rubber seed and palm oil seed from which the oil is extracted chemically or mechanically (IEA Energy Technology Essentials, 2007). Chemically vegetable oils and animal fats have triglycerides consisting of three fatty acid chain ester bounded to glycerol molecule. The main reason of not using these oils directly as an engine fuel is high viscosity, which effects the engine performance badly by choking the injectors and undesirable carbon deposits in the combustion chamber because of the polymerization due to unsaturation (Dhar et al., 2012).The alcohol used in alcoholysis can be methanol, ethanol, propanol, butanol. Methanol being a short chain alcohol is preferred because of its low cost and its physiochemical advantages (Balat and Balat, 2010). Transesterification is an equilibrium limited reaction that why excess alcohol is required to shift the reaction equilibrium towards product side. Increase in reaction temperature increases the methyl ester yield but if the temperature exceeds the boiling point of alcohol the

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concentration of methyl esters will decrease because most of the alcohol will be in vapor phase and there is insufficient liquid-liquid interaction (Morshed et al., 2011).

Fatty acids are a component of both vegetable oil and biodiesel. In chemical terms, they are carboxylic acids as was shown in Fig. 1a.

Fatty acids which are not bound to some other molecule are known as free fatty acids. When reacted with a base, a fatty acid loses a hydrogen atom to form soap as was shown in Fig. 1b.

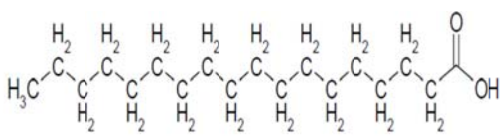
Chemically, soap is the salt of fatty acid. The structures of fatty acids shown in this section are highly idealized. Real fatty acids vary in the number of carbon atoms, and in the number of double bonds. Glycerol, a component of vegetable oil and a by-product of biodiesel production as was shown in Fig. 1c.

Alcohols are organic compounds of the form R-OH, where R is a hydrocarbon. Typical alcohols used in biodiesel-making are methanol, ethanol, 1-propanol, and 1-butanol as was shown in Fig. 1d

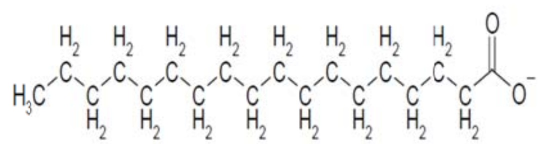
Among these, methanol is most commonly used to make biodiesel. Since ethanol is easily obtained from plant sugars, while methanol is commonly produced from natural gas, using ethanol makes for a more sustainable fuel. Ethanol is harder to use because it forms emulsions easily, making the separation of end products more difficult.

Transesterification is sometimes called alcoholysis, or if by a specific alcohol, by corresponding names such as methanolysis or ethanolysis. Chemically, biodiesel is a fatty acid alkyl ester as was shown in Fig. 1e and an ester is a compound as was shown in Fig. 1f.

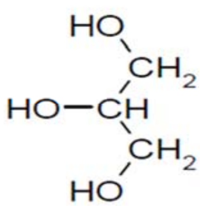
The biodiesel ester contains a fatty acid chain on one side, and a hydrocarbon called an alkane on the other. Thus, biodiesel is a fatty acid alkyl ester. Usually, the form of the alkane is specified, as in "methyl ester" or "ethyl ester". Vegetable oil is a mixture of many compounds, primarily triglycerides and free fatty acids. A triglyceride is a tri-ester of glycerol and three fatty acids as was shown in Fig. 1g.



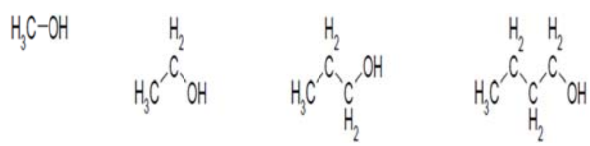
(a): Molecular Structure of Idealized Fatty Acid



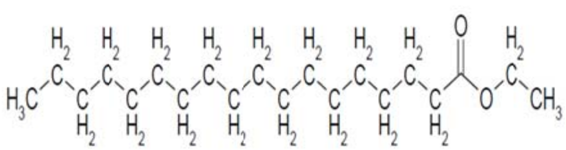
(b): Molecular Structure of Soap



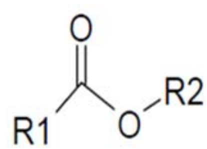
(c): Molecular Structure of Glycerol



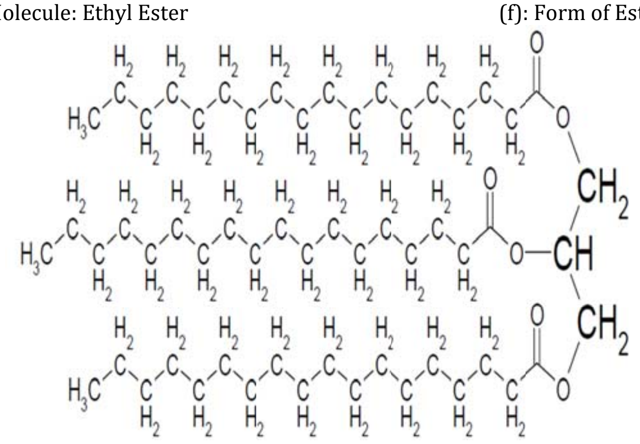
(d): Molecular structure of methanol, ethanol, 1-propanol, and 1-butanol



(e): Biodiesel Molecule: Ethyl Ester



(f): Form of Ester Compound



(g): Molecular Structure of Triglyceride

Fig. 1: Form of carboxylic acids

Transesterification is an equilibrium limited reaction, excess alcohol is required to shift the reaction equilibrium towards product side. Increase in reaction temperature increases the methyl ester yield but if the temperature exceeds the boiling point of alcohol the concertation of methyl esters will decrease because most of the alcohol will be in vapour phase and there is insufficient liquid-liquid interaction (Morshed et al., 2011).

Biodiesel, a type of biofuel has been studied and optimized to obtain kinetic reaction model. However, currently the kinetic reaction models present for biodiesel production are limited to specific reactions involved in biodiesel production. Therefore, study of reactions involved in the biodiesel production is very important. There is need of development of a general reaction kinetic model by which we can calculate the reaction kinetics data for reactions involved in biodiesel production

To study the reaction kinetics there were several kinetic models developed in the past years based on specific trans-esterification reactions. The development of kinetic reaction model began by Freedman and colleagues at USDA in the early 1980's about the trans-esterification reaction of soybean oil and other vegetable oils with butanol and alcohols. The effects of the type of alcohol, molar ratio, type and amount of catalyst and reaction temperature on rate constants and kinetic order are studied by Liu (2013). Kinetic study was also carried out under non-catalytic conditions. Kusdiana and Saka (Kusdiana and Saka, 2001) studied the kinetics of transesterification of rapeseed oil to biodiesel fuel without the application of a catalyst in supercritical methanol.

In the present study reaction kinetic model is being developed to study the kinetic parameters and to find the rate constants of transesterification reaction to produce biodiesel and validated the model by comparing three experimental results with the simulation results from MTALAB optimization tool box.

2. Materials and methods

2.1. Biodiesel production

Biodiesel or alkyl ester is a type of biofuel produced from vegetable oil and fats with the addition of alcohol and the use of catalyst through primarily the process of trans-esterification producing glycerol as co-product.

Trans-esterification reaction can be represented as follows (Fig. 1 and Table 1-3):

$$TG + ROH \overset{k_1,k_2}{\longleftrightarrow} DG + RCO_2R_1$$
$$DG + ROH \overset{k_3,k_4}{\longleftrightarrow} MG + RCO_2R_2$$
$$MG + ROH \overset{k_5,k_6}{\longleftrightarrow} GL + RCO_2R_3$$
$$TG + 3ROH \overset{k}{\leftrightarrow} 3ME + GL$$

Fig. 1: Process flow chart

Where k_1, k_3 and k_5 are the rate constants for forward reactions; k_2, k_4 and k_6 are rate constants for reverse reactions; ROH is alcohol; RCO_2R_1, RCO_2R_2 and RCO2R3 are fatty acid esters; TG, DG and MG are Triglycerides, Diglycerides and Monoglycerides respectively. ME is Methyl Ester and GL is Glycerol (Okullo et al., 2010).

3. Results and discussions

Experimental results were used as initial results to compare with the simulation in MATLAB.

Table 1: Comparison of Experimental (Dhanasekaran, 2012) with Simulation results at reaction temperature 328 (k) using MATLAB

Components	Units	Temperature (k)	
		328	
		Experimental Results	Simulation Results
Diglycerides	% w/w	4.6	4.6
Monoglycerides	% w/w	3.6	3.6
Glycerol	% w/w	6.9	20.8
Methyl Esters	% w/w	85	82

Table 2: Comparison of experimental (Dhanasekaran, 2012) with Simulation results at reaction temperature 333 (k) using MATLAB

Components	Units	Temperature (k)	
		333	
		Experimental Results	Simulation Results
Diglycerides	% w/w	3.8	3.4
Monoglycerides	% w/w	2.1	2.1
Glycerol	% w/w	7.2	21.0
Methyl Esters	% w/w	94	95

Table 3: Comparison of experimental ((Dhanasekaran, 2012) with Simulation results at reaction temperature 338 (k) using MATLAB

Components	Units	Temperature (k)	
		338	
		Experimental Results	Simulation Results
Diglycerides	% w/w	3.2	2.8
Monoglycerides	% w/w	1.2	1.5
Glycerol	% w/w	9.1	21.6
Methyl Esters	% w/w	95	96

3.1. Model validation

Feed stock : Palm Oil
Oil/Methanol Ratio : 6
Potassium Hydroxide : 0.45 % w/w (catalyst)

The experimental and the simulation results showed that on increasing the reaction temperature reduces the concentration of Diglycerides in the product as increased temperature increased the rate of reaction as shown in Fig. 2(a).

The experimental and the simulation results show the decreasing trend of monoglycerides against temperature as shown in Fig 2 (b).

The higher the reaction temperature higher will be the conversion of monoglycerides to methyl esters because high temperature favors the conversion by increasing the rate of reaction, reduces the concentration of monoglycerides in the product. As conversion of monoglycerides increases, more pure is the product obtained as shown in Fig. 2(c). The increase in the reaction temperature increases the methyl esters concentration in the product.

Glycerol is the byproduct obtained during transesterification reaction. As the conversion of glycerides increases there is also an increase in the concentration of the glycerol along with the product as shown in Fig 2(d).

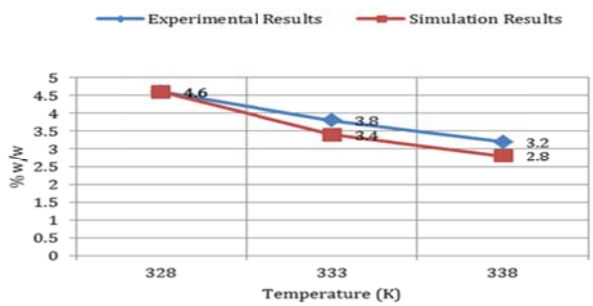


Fig. 2(a): Graph of comparison between experimental results and simulation results based on composition of diglyceride against temperature

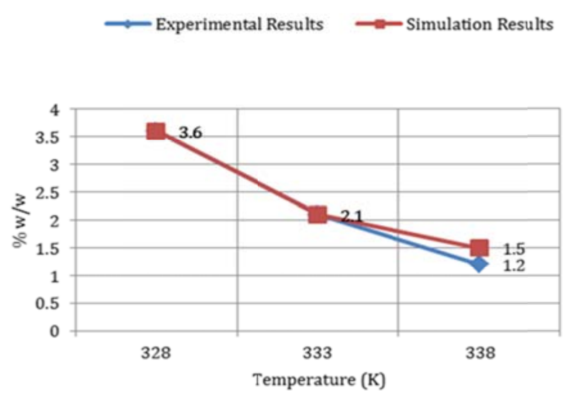


Fig. 2(b): Graph of comparison between experimental results and simulation results based on composition of monoglyceride against temperature

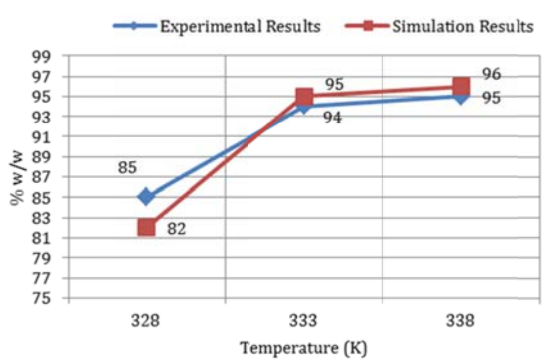


Fig. 2(c): graph of comparison between experimental results and simulation results based on composition of methyl esters against temperature

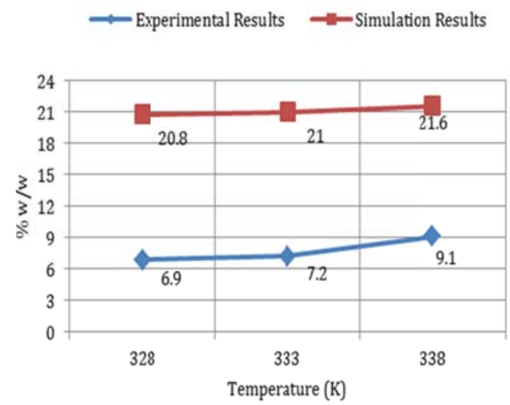


Fig. 2(d): Graph of comparison between experimental results and simulation results based on composition of glycerol against temperature

Experimental and Simulation Results in Fig. 2 show the decreasing trend in terms of concentrations of Diglycerides, Monoglycerides and shows increase in the concentration of the product with increase in temperature.

The simulation results yield the similar set of results compared to experimental results in terms of composition of Diglycerides, Monoglycerides and Methyl Esters in the transesterification reaction of palm oil with potassium hydroxide (KOH) as catalyst in the reaction. The set of results generated from MATLAB Simulation vary from the experimental results with minimal error which is below 5% error.

Fig. 2(d) shows increase in terms of percentage composition of glycerol as the experimental results shows concentration values of 6.9, 7.2 and 9.1 for temperatures of 328K, 333K and 338K respectively whereas MATLAB Simulation shows concentration values of 20.8, 21.0 and 21.6 for temperatures 328K, 333K and 338K respectively.

3.2. Rate constants optimization

Fig. 3 shows the rate constants developed for each step of reaction from MATLAB optimization values of activation energy and pre-exponential. The results shows increase in the k value as k depends directly on rate of reaction, due to this increase in temperature increases the value of rate constant. A total of three runs have been carried out to develop and validate a general reaction kinetic model. From the results obtained from the three runs in MATLAB OPTIMIZATION TOOLBOX, there have been similar set of results generated when compared to the actual experimental results with error of less than 5% in terms of production of methyl esters (Biodiesel). Although, there have been slight increase in concentration in terms of composition of Glycerol in the product, the methyl esters yield from the simulation in MATLAB shows similar results with experimental results in all the three runs and thus validate the model (Table 4).

Table 4: Simulation Results from MATLAB OPTIMIZATION TOOLBOX

Components	Temperature (k)		
	328	333	338
Rate Constant (k) 1	1.187	1.199	1.210
Rate Constant (k) 3	0.772	0.792	0.812
Rate Constant (k) 5	0.189	0.200	0.210
Pre-exponential Factor (A) 1	2.214	2.214	2.214
Pre-exponential Factor (A) 3	4.269	4.269	4.269
Pre-exponential Factor (A) 5	6.392	6.392	6.392
Activation Energy (E) 1	204.33	204.33	204.33
Activation Energy (E) 3	561.073	561.073	561.073
Activation Energy (E) 5	1154.072	1154.072	1154.072

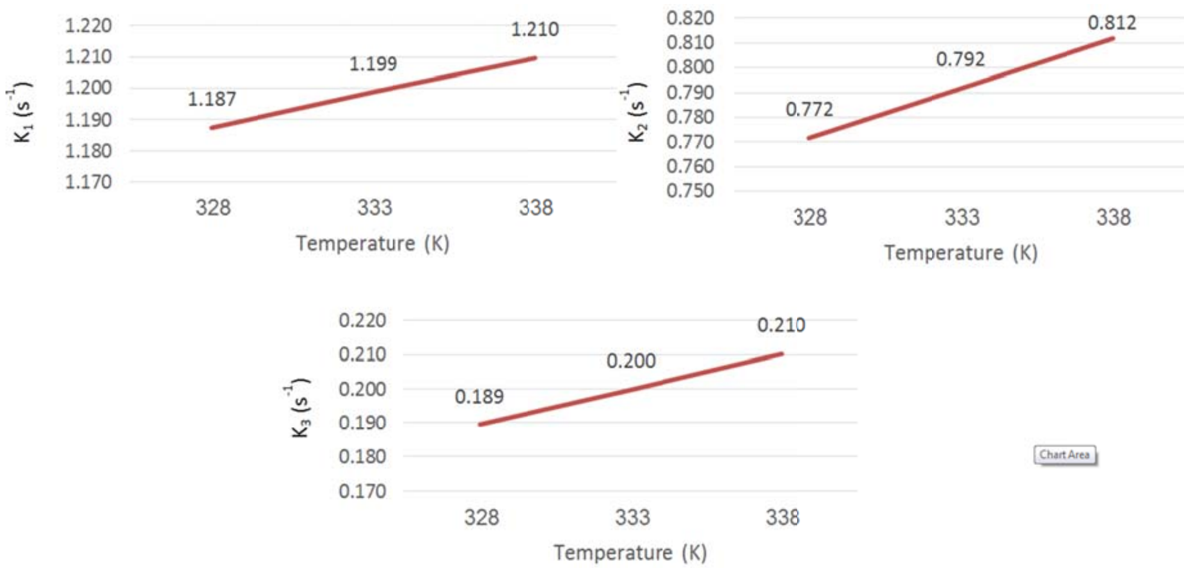


Fig. 3: Graph of Simulation Results based on Rate Constant k1, k3, k5

Furthermore, the optimized value of activation energy and the pre-exponential factor values are general values that can be used at any temperature to calculate the concentration of the product yield. This enables to use the optimized values to calculate the rate constants at any temperature.

4. Conclusion and recommendation

As a conclusion, a general kinetic model and parametric study of the kinetics of the reaction involved in the synthesis of biodiesel developed by using MATLAB OPTIMIZATION TOOLBOX have shown promising results whereby it has the potential to yield the similar set of results compared to experimental results. Despite the increase in concentration of glycerol and the rate constants, the methyl esters yielded similar results with minimal error below 5 %. The work can further be improved by carrying out real experiments to prove the validity of the model by expanding the parametric study to the amount of catalyst, and the reaction time.

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