

Biodiesel Production via Esterification of Free Fatty Acids from *Cucurbita pepo* L. Seed Oil: Kinetic Studies

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ABSTRACT

Due to high free fatty acid content of most traditional biodiesel feedstock, studies were carried out to optimize biodiesel production via esterification of free fatty acid from *Cucurbita pepo* seed oil. The experiments were carried out with methanol and butanol in a batch reaction system at 6:1 volume ratio of alcohol/FFA. H_2SO_4 was used as the catalyst. Various kinetic parameters such as quantity of catalyst, effect of stirring rate, reaction temperature and time were studied with aim of determining the best possible conditions. Attempt was made to fit our experimental data into first and second order kinetics to verify the best possible order of the reactions. Activation energy was determined by plot of $\ln K$ versus $1/T$. From the correlation coefficients (R^2), the best kinetic model for our data appeared to fit first order for butylation and second order for methylation. Activation energies of 39.91KJ/mol and 35.54KJ/mol were determined for the butylation and methylation reactions respectively.

Keywords: Biodiesel, Kinetics, *Cucurbita pepo* Seed oil, Esterification.

1. INTRODUCTION

Liquid biofuels are being increasingly considered as alternatives to gasoline and diesel fuel as energy sources owing to their potential to reduce numerous environmental stress caused by fossil fuel use. Biodiesel has similar fuel properties to diesel and therefore it can be used as a substitute for diesel fuel, either in neat form or in blends with petroleum diesel (Pasiak *et al.*, 2006). It has the following advantages over petroleum-based diesel; it is renewable, carbon neutral, more rapidly biodegradable, less toxic, has a higher flash point and low sulfur content. Availability of feedstock and optimization of production process are, however, among the biggest challenges facing biofuel industry worldwide. In most parts of Nigeria, *Cucurbita pepo* is cultivated mainly for the fruits and the leaves which are used as vegetable. The seed oil has no known commercial application yet. Therefore, in the search for alternative oils for biodiesel production, *Cucurbita pepo* seed oil presents a promising choice. Among the culinary applications of the seed oil includes, it serves as a salad dressing when combined with honey or olive oil. The oil is not commonly used for cooking (Schinas *et al.*, 2009) probably because cooking the oil destroys its essential fatty acids.

The suitability of the *Cucurbita pepo* seed oil for biodiesel production has already been investigated. Ajiwe *et al.*, 2006 studied the biofuel properties of the methyl esters of the seed oil and Schinas *et al.*, 2009 also investigated the FAME of the oil as an alternative diesel fuel in Greece. Both studies recommended the oil as a good feedstock for biodiesel production. However, there

is no information available on the chemical kinetics of the transesterification of the seed oil as at the time of this work.

Commercial biodiesel is currently based on base-catalysed transesterification of vegetable oil. Very often, the transesterification is carried out using homogeneous catalysts such as KOH, NaOH. These catalysts are susceptible to production of unwanted by-products such as soap when the base oil contains high free fatty acids and water. The soap formation reduces catalyst activity, biodiesel yields and compromises easy separation of the product after production. As a result, the quality of the feed oil in this process must be low in moisture and fatty acids to attain higher process yields and prevent the formation of undesired by-products. Since most crude vegetable oils do not meet this condition, refining of the oil before transesterification becomes necessary and this increases production costs.

Some of the approaches adopted for processing oils with high moisture and/or free fatty acid contents include; the use of supercritical methanol to convert the oil at high temperature (Saka *et al.*, 2001), a simultaneous esterification/transesterification of the FFAs and triglyceride contents of the oil using acid catalyst, and a two-step sulfuric acid-catalyzed pre-esterification before base-catalyzed transesterification (Canakci *et al.*, 2001). Also another two-step process involves a complete hydrolysis of the oil with subcritical water at 270°C and subsequent methyl esterification of the resulted FFAs at the same temperature (Kusdiana *et al.*, 2004). Hydrolysis/esterification process for biodiesel production

has advantage of incorporating feedstock purification and the reaction time is always short compared to conventional transesterification reactions.

The focus of this project was to characterize the reaction kinetics of esterification of *Cucurbita pepo* with a view to optimizing the reaction process at alcohol/FFAs ratio of 6:1.

2. MATERIALS AND METHOD

2.1 Collection and Preparation of Materials

Cucurbita pepo fruits were collected from a farm at Emene. The seeds were removed, washed and sun-dried for 7 days. It was later ground and stored in air-tight plastic containers. The oil from the ground sample was thoroughly extracted with petroleum ether using a soxhlet extractor. The acid value of the extracted oil was determined using 0.05M alcoholic KOH and was found to be 26.32mgKOH/g. This indicated that it could not be processed directly using base-catalyst transesterification. The chemicals used in the experiment include, sulfuric acid (98 %wt), sodium hydroxide pellet of 98.2% purity, methanol and butanol (analytical grade reagents).

2.2 Conversion of the Oil to Free Fatty Acids

The oil was completely hydrolysed into free fatty acids by the method described in Ajiwe *et al.*, 2001. It was first converted to soap and by gradual addition of some quantities 1:3 sulphuric solution, the free fatty acids in the soap was released. The free fatty acids generated was washed with warm distilled water and used for the kinetic studies.

2.3 Reaction Condition

Esterification of the FFAs was carried out using methanol and butanol separately in the presence of concentrated sulfuric acid as the catalyst in a batch process. 250ml conical flask equipped with reflux condenser, magnetic stirrer was used as the reactor. The reactor was immersed in a water bath (1000ml beaker containing 200ml water and thermometer) to maintain a uniform temperature on heating. The heating was done by digital magnetic heater. The alcohol/FFAs ratio was fixed at 6:1 throughout the process. This was because previous investigations indicated a maximum conversion at that ratio. Effect of temperatures between 40 to 80°C was studied. Catalyst amount was varied between 0.5 to 5% by weight, and the stirring rate was varied between 0 to 800 rpm to ascertain their effect on the biodiesel yield.

The progress of the reaction was monitored by withdrawing some samples from the reactor at interval of time, washing it with distilled water to remove the unreacted alcohol and residual acid catalysts and then

titrating against 0.05M alcoholic KOH (Pasiyas *et al.*, 2006; Berrios *et al.*, 2007; 2009; Alípio *et al.*, 2009; and Abiney *et al.*, 2008).

$$\% \text{Conversion} = \frac{(A_0 - A_t) \times 100}{A_0} \quad (1)$$

Where;

A_0 = initial acid value

A_t = acid value after the time, t.

During the washing, litmus paper was used to confirm complete removal of the residual catalyst before titration; the sample must be neutral to litmus paper to indicate a complete absence of the acid catalyst.

3. RESULTS AND DISCUSSION

3.1 Effect of Quantity of Catalyst

The effect of catalyst was studied at 70°C, alcohol/FFAs ratio of 6:1 and stirring rate of 260rpm. From the results in Fig.1, the %conversion of the FFAs to biodiesel increased with increase in quantity of catalyst and reached optimum at 3% for both methyl and butyl esterification as further increase in catalyst concentration showed no further increase in the %conversion.

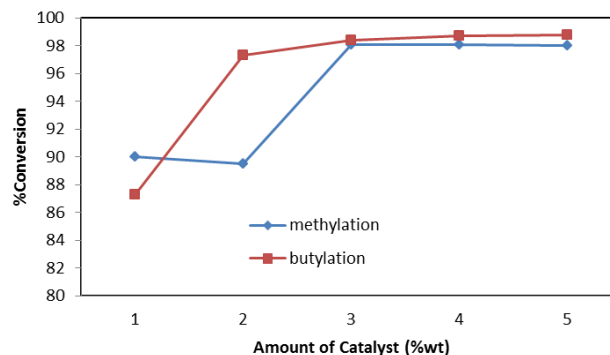


Fig.1: Effect of quantity of catalyst at alcohol/FFAs ratio of 6:1, 70°C and stirring rate of 260rpm

3.2 Effect of Reaction Temperature

The effect of temperature on the %conversion of the FFAs to methylesters and butylesters was also studied at alcohol/FFAs volume ratio of 6:1 and agitation rate of 260rpm for 60min. Temperatures of 28°C, 40°C, 50°C, 60°C, 70°C and 80°C were studied. It was observed that temperature had a prominent effect on the %conversion (Fig.2). The rate of reaction increased with increase in temperature and reached optimum at 50°C for methylation and increased up till 80°C for butylation. Reaction temperature near the boiling point of the alcohol was recommended for faster conversion by various literatures

and our result was in agreement with this. At room temperature, there was up to 78% conversion after 60 minutes, and this indicated that the methyl esterification of the FFAs could be carried out appreciably at room temperature but might require a longer reaction time. In butyl esterification, however, temperature had stronger influence. At 80°C, there was 92.46% conversion as against 98.20% in methyl esterification. Temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in much faster reactions. The influence of temperature on the miscibility of alcohol and oil phases was more pronounced in butylation.

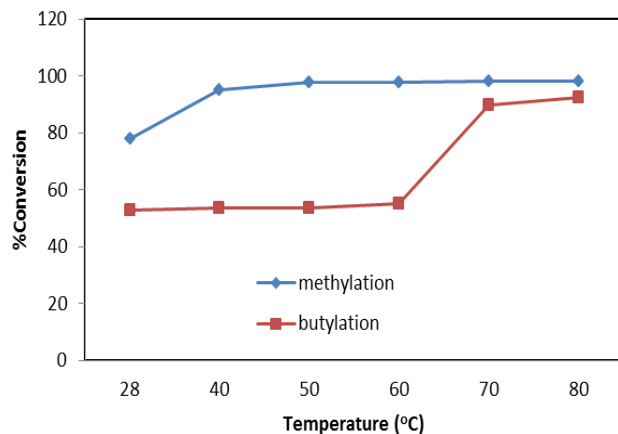


Fig.2: Effect of temperature at alcohol/oil ratio of 6:1 and stirring rate of 260rpm

3.3 Effect of Time on the %Conversion

At 70°C, alcohol/FFAs volume ratio of 6:1, stirring rate of 260rpm and using the optimum catalyst, %conversion of the FFAs as a function of time was studied. Fig.3 showed the kinetic curves. The result revealed that the reaction rate was more rapid at the initial stages and retarded as the reaction progressed. Within the 10min. of methyl esterification, there was about 97% conversion, and the rate later diminished and attained equilibrium at about 30min. The rate of butyl esterification, however, was slower. This could be explained from the molecular size of the alcohols. According to theory of reaction rate, before a chemical reaction occurs, the reacting species must collide with one another with sufficient energy. The collision must occur with appropriate orientation, that is, it must be capable of bringing the reactive sites together. The more complex a molecule is the less chance of colliding with appropriate orientation and the slower the reaction rate. Butanol is more complex than methanol and this is attributable to the observed slower reaction rate of butyl esterification compared to methyl esterification. The result is in accordance with the findings of previous researchers. Alípio *et al.*, 2009 reported that alcohol reactivity followed the order methanol > ethanol > isopropanol.

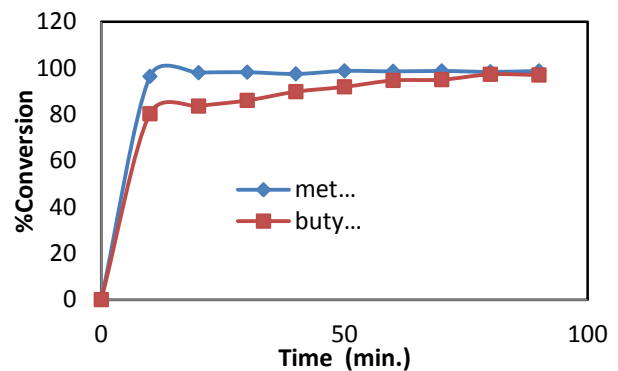


Fig.3: Effect of time on %conversion at alcohol/FFAs ratio of 6:1, 70°C and stirring rate of 260rpm

3.4 Effect of Stirring Rate on %Conversion of the Oil Biodiesel

Fig.4 showed the effect of stirring rate on methyl and butyl esterifications of the FFAs at 70°C and alcohol/FFAs ratio of 6:1 for 60min. The %conversion increased with increase in stirring rate and reached saturation at 400rpm for butylation and 200rpm for methylation. Greater agitation rate required for butylation could be attributed to higher viscosity of butanol compared to methanol.

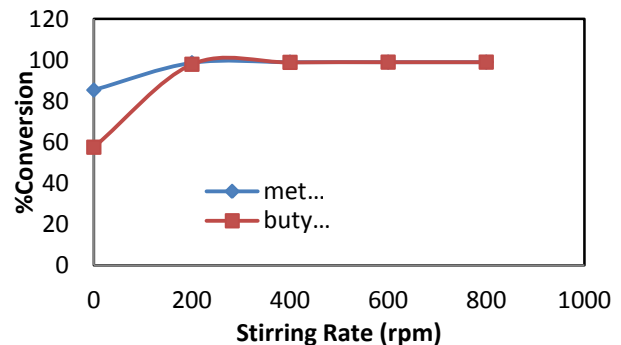


Fig.4: Effect of stirring rate on the %conversion at 70°C alcohol/FFAs ratio of 6:1 and 70°C

3.5 The Reaction Kinetics

In order to design an efficient continuous reactor for biodiesel production from *Cucurbita pepo*, a suitable kinetics mechanism and reaction rate constants is necessary. Several literature data attributed a pseudo first order dependence for esterification of fatty acid especially at high alcohol/FFAs ratio (Silva *et al.*, 2008). However, second order dependence had also been reported (Tanaka *et al.*, 2001). One of the main objectives of this study was to verify the possible reaction order which the esterification reaction obeyed at alcohol/FFAs ratio of 6:1. The knowledge of this would provide a functional relationship between concentration and the reaction rate. The experimental results were fitted into first and second

order kinetic model, and through the correlation coefficients, the order that best fit our data was identified.

Equation 2 describes variation of concentration of the substrate with relation to time for first order kinetics (Abiney *et al.*, 2008) and a Plot of $\ln[A]$ versus reaction time would give a straight line with a slope equals to $-k_1$.

$$\ln [A]_t = -kt + \ln [A]_0 \quad (2)$$

Where $[A]_0$ and $[A]_t$ represent initial concentrations of FFAs and the concentration after a time, t , respectively.

For second order verification, a plot of reaction time versus $1/[A]$ was made and the slope is equal to K_2 . Table 1 showed the results of the overall rate constants and the corresponding correlation coefficients. Fig. 5 and 6 showed examples of plots for verification of first and second order kinetics.

From the correlation coefficients (R^2), the best kinetic model for our data appeared to be a pseudo first order for butylation and second order model for methylation.

Table 1: The Overall Rate Constants and the Correlation Coefficients (R^2) on Methylation

Reaction	Temperature (°C)	1st Order Rate Constant K_1 (min. ⁻¹)	R^2	2nd Order Rate Constant K_2 (g/mgKOH.min)	R^2
Methylation					
	40	0.066	0.953	0.005	0.915
	50	0.102	0.840	0.044	0.965
	60	0.111	0.716	0.087	0.830
	70	0.103	0.687	0.090	0.928
Butylation					
	40	0.013	0.986	0.000	0.983
	50	0.027	0.954	0.000	0.941
	60	0.043	0.977	0.002	0.886
	70	0.046	0.957	0.002	0.934

The overall rate constants for first order verification were 0.013, 0.027, 0.043 and 0.046 (g/mgKOH.min) at 40, 50, 60 and 70°C for butylation with corresponding correlation coefficients of 0.986, 0.954, 0.977 and 0.957. The correlation coefficients were generally higher than that of second order for butylation and this indicated that the reaction obeyed first order. On the other hand, the reverse was the case for methylation. Although, several literatures attributed first order kinetics to esterification of FFAs with methanol, the studies were carried out at higher alcohol/oil ratio (Silva *et al.*, 2008).

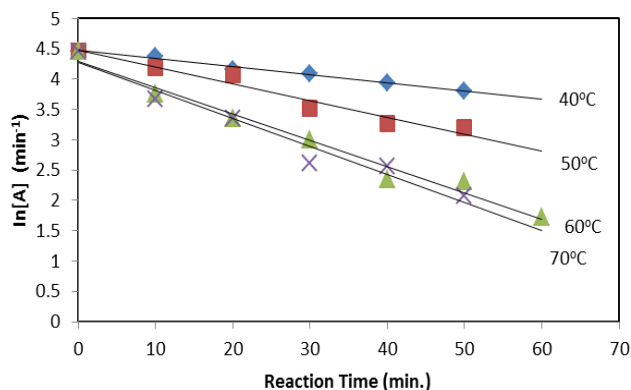


Fig.5: Verification of first order kinetics for butylation

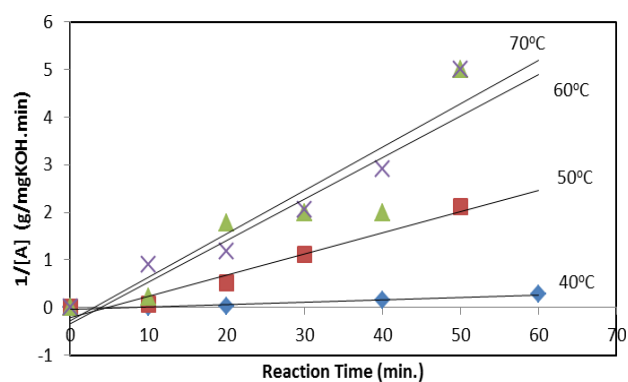


Fig.6: Verification of second order kinetics for methylation

Furthermore, the values of the overall rate constants obtained were used to determine the activation energy (E_a) following Arrhenius equation (3). A plot of $\ln k$ versus the reciprocal of absolute temperature was made and a straight line with a slope equal to $(-E_a/R)$ was obtained (Fig.7).

$$\ln k = (-E_a/R) / T + C \quad (3)$$

Where E_a is the activation energy, R is the gas constant, k is overall rate constant and C is a constant.

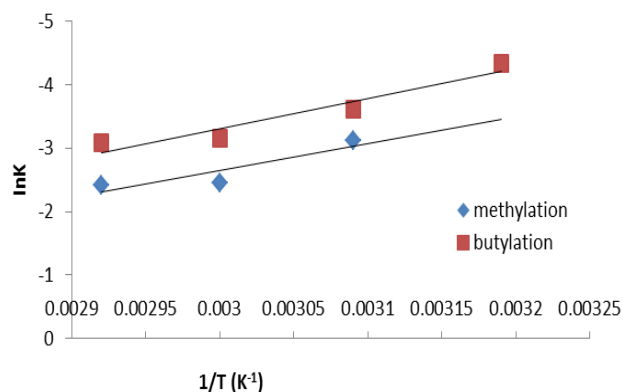


Fig. 6: Arrhenius plot of reaction rate with reciprocal temperature

Table s: Activation Energies

Reaction	E_a (KJ/mol)	R^2
Methylation	35.54	0.812
Butylation	39.91	0.919

The activation energy for methylation of the FFAs was found to be 35.54KJ/mol while that of butylation was 39.91KJ/mol. Methylation of the FFAs had lesser energy of activation than butylation. Activation energy is the minimum amount of energy which reacting molecules must possess before a reaction can occur. The lower activation energy of methylation compared to butylation implied that methanol molecules were easily activated than butanol molecules.

4. CONCLUSION

Cucurbita pepo seed oil presents a promising choice for biodiesel production in Nigeria. However, due to inherent high FFAs content of most of crude vegetable oils, the knowledge of esterification kinetics becomes important for optimal biodiesel production from the feedstock. The focus of this work was on the optimization of biodiesel production from *Cucurbita pepo* seed oil via esterification of FFAs. At alcohol/oil ratio of 6:1, 3% by weight of catalyst (H_2SO_4) and stirring rate of 200 and 400rpm was found to be optimal for methylation and butylation respectively. Reaction temperature of 50°C was as well found sufficient for the methyl esterification reaction while for butyl esterification, higher temperature was required. First order kinetics was proposed for butylation and second order for methylation according to our experimental data.

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