

Compensation Effect in Transesterification Kinetics of Croton Megalocarpus Oil using Heterogeneous Alkaline Earth Catalysts

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Abstract - Reaction kinetics of transesterification of croton megalocarpus oil with methanol to produce fatty acid methyl ester was studied at 70°C, using homogeneous and heterogeneous catalysts through conventional heating and microwave irradiation. NaOH was used as a homogenous catalyst, and alkaline earth metal oxides, BaO, SrO, CaO, MgO and BeO, were the heterogeneous catalysts. Reaction rate constant k ; and Arrhenius equation parameters, pre-exponential factor A and activation energy E were estimated from kinetic data, using the overall reaction. By considering the magnitudes of k , NaOH was the most active catalyst, followed by BaO, SrO, CaO, MgO and BeO. However, no specific order was observed in the estimated values of A and E . Activation energy was not found to be a direct measure of catalyst activity for heterogeneous catalysts. This was explained by the complex nature of the three-phase reaction system where twenty one reactions were likely to be taking place simultaneously, and the observed kinetic parameters were the overall apparent values. Cremer Constable scatter plot showed the data points roughly following a straight line. It was concluded that the discrepancies in A and E values were due to oversimplification of kinetic model, rather than being a physical phenomena.

Key Words: Transesterification, Croton megalocarpus, Alkaline earth oxides, Kinetics, Conventional heating, Microwave irradiation, Compensation effect, Cremer Constable plot.

1. INTRODUCTION

Biodiesel is a biofuel obtained from renewable sources and is recognized as an alternative to petro-diesel. In 2014 biofuels provided 4% of the fuel for transport sector, which is to rise to 4.3% in 2020. Reduction in petroleum crude prices in 2014 affected the production and use of

biofuels. Production in 2014 was 126 billion litres, expected to rise to 144.5 billion litres in medium terms to year 2020 [1]. In spite of the recent discoveries of new crude sources, especially in Africa; petroleum reserves are finite, and would deplete or exhaust. It is estimated that the world is consuming 2.7% of petroleum reserve annually, and the stocks would last about 50 years [2]. Another advantage of biofuels is their superior environmental footprint. Biofuels consist of mainly carbon, hydrogen and oxygen. Upon combustion, these fuels are carbon neutral, do not produce nitrogen and sulphur oxides, unlike petroleum derived fuels. Biodiesel fuel produces far lower emissions of unburned-hydrocarbons, carbon dioxide, carbon monoxide, sulphates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, ozone forming hydrocarbons and particulate matters [3]. Greenhouse gas emissions from biodiesel are between 22 and 59% of the emissions from petro-diesel. [4]. Biodiesel is produced by reacting vegetable oils or animal fats with an alcohol in presence of a catalyst. The reaction is a transesterification reaction producing alkyl ester (biodiesel) and glycerol.

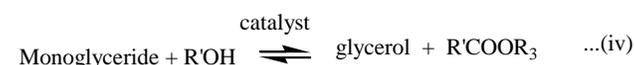
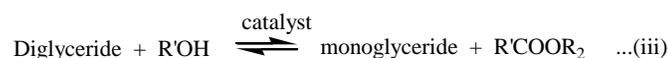
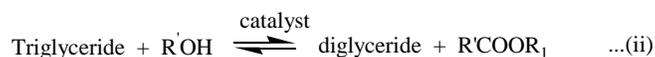
1.1 Transesterification reaction

In a transesterification reaction of a triglyceride (oils and fats) alcohol is displaced from the triglyceride ester by another alkyl alcohol to produce an alkyl ester (biodiesel) and glycerol. The overall reaction can be represented as follows:



When methanol is used as alkyl alcohol, the corresponding alkyl ester is fatty acid methyl ester (FAME). The above reaction is a reversible reaction, and is usually carried out in presence of a catalyst. Reaction (i) is the overall reaction, supposed to take place in three steps. In the first step, triglyceride reacts with alcohol to produce diglyceride and ester. Further reaction with alcohol produces monoglyceride and ester (second step), followed by reaction of monoglyceride with alcohol to produce

glycerol and ester (third step). The three reaction steps are as below:



In the above reactions, R' is the alkyl group for the alcohol whereas R₁, R₂ and R₃ are carbon chain of fatty acid [5]. Catalysts used for the transesterification reaction can be homogenous or heterogeneous. Homogeneous catalysts are acids, bases and enzymes. Homogeneous basic catalysts such as sodium hydroxide, alkali metal alkoxides and potassium hydroxide, are generally preferred due to their higher activity. Homogenous catalysts cannot be recovered during the process, and therefore cannot be recycled. Neutralizing and washing of these catalysts are a major process steps, which adversely affects the economic viability and environmental impact. Heterogeneous catalysts, on the other hand, can be recovered and recycled, and are more environmental friendly.

1.2 Heterogeneous catalysts

Heterogeneous catalysts are classified as single component metal oxides, zeolites, supported alkali metals, clay minerals and non-oxides [6]. These catalysts are highly selective and their activity mostly depends on their surface properties [7]. Similar to homogenous basic catalysts, heterogeneous basic catalysts too give a higher reaction rate. Single component basic metal oxides have been extensively studied for transesterification. Alkaline earth metal oxides, BaO, SrO, CaO, MgO, BeO have been used in pure form, or supported on a porous base. Surfaces of these basic oxides are covered with water and carbon dioxide, and they also form carbonates and hydroxides when exposed to atmosphere. A pre-treatment at high temperature is usually required to remove adsorbed species, and to break hydroxides and carbonates back into oxides [8], [5]. Transesterification reaction kinetics were studied for croton *megalocarpus* oil and methanol reaction employing BaO, SrO, CaO, MgO and BeO catalysts.

1.3 Reaction kinetics with alkaline earth metal oxide catalysts

Reaction system consists of three immiscible phases- oily, aqueous and solid; composed of triglyceride, FAME, glycerol, methanol, and catalyst. This poses severe mass transfer and surface reaction challenges. In a solid-liquid-liquid system, the resistance to reaction could be due to seven steps [9]: (1) Diffusion of reactant molecules through bulk liquid phase to catalyst surface, (2) Diffusion of reactant molecules through liquid-solid surface or catalyst pore, (3) Adsorption of reactant molecules on catalyst active sites, (4) Chemical reaction at catalyst surface, (5) Desorption of product molecules from catalyst active sites (6) Diffusion of product molecules through liquid-solid surface or catalyst pore, (7) Diffusion of reactant molecules through catalyst surface to bulk liquid phase. Slowest of these seven steps, controls the reaction rate. These seven steps occur in the three transesterification reactions, (ii), (iii) and (iv) given above, resulting into overall twenty seven reaction steps. Langmuir-Hinshelwood mechanism for a solid- fluid reaction, for two reactants and two products, consists of five reaction steps, chemisorption of the two reactants, surface reaction, desorption of the two products [6]. Another mechanism for solid-fluid reactions is Eley-Rideal mechanism which has similar reaction steps. For transesterification reaction, Langmuir-Hinshelwood mechanism is preferred [10]. This emphasises the complex nature of reaction steps, which makes it practically impossible to study a single intermediate reaction. The observed reaction parameters are, therefore, the net result of these numerous transport/ reaction steps.

1.3.1 Reaction rates, activation energy and pre-exponential factor

Chemical reaction rate constant, k , is a temperature dependent term. The temperature dependency is well represented by Arrhenius' law [11]:

$$k = k_0 e^{-E/RT} \quad \dots(\text{v})$$

where k_0 is called the frequency factor (or pre-exponential factor, A) and E is called the activation energy of the reaction. T is the temperature and R is universal gas constant.

An alternate expression of Arrhenius' law is:

$$k = k_0' T^m e^{-E/RT} \quad 0 \leq m \leq 1 \quad \dots(\text{vi})$$

The exponential term in the above equation (vi) is so much more temperature-sensitive than the T^m term, the variation of k caused by the later is effectively masked, and the expression reduces to equation (v). Equation (v), in logarithmic form is:

$$\ln k = \ln k_0 - E/RT \quad \dots(\text{vii})$$

Hence a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $(-E/R)$. Frequency factor k_0 is also known as pre-exponential factor denoted by A .

A catalyst lowers the activation energy of a reaction, but the magnitude of activation energy for a heterogeneously catalysed reaction is not automatically accepted to be a quantitative measure of the catalytic activity. The reason for not adopting this criterion is the widespread occurrence of compensation effects [12]. For heterogeneous catalysis compensation effect may occur when the overall reaction is a combination of a number of reactions which show the same mechanism and take place on different groups of active centres, each group showing different activation energy and pre-exponential factor [13]. Transesterification reaction consisting of three consecutive reactions falls under this category. Reaction velocity constant in this case is a sum of several reaction steps, and activation energy is termed 'apparent activation energy', E^{app} , and pre-exponential factor is termed 'apparent pre-exponential factor', A_{app} . In some reaction systems, it has been observed that the apparent activation energy varies under different reaction conditions. It is also found that the variation in apparent activation energy is accompanied by a change in A_{app} , i.e., a large apparent activation energy is accompanied by a large apparent pre-exponential factor and vice versa. In some cases, the changes in apparent pre-exponential factor and apparent activation energy display a linear dependency according to the Cremer-Constable relation [14]:

$$\ln A_{app} = a E^{app} + b \quad \dots(\text{viii})$$

The relation implies that values of the natural logarithm of the prefactor plotted against the apparent activation energy (denoted a Constable plot), as obtained from an Arrhenius plot, fall on a straight line with slope a and intercept b . Although the compensation effect has been known and studied for a very long time, especially in the field of heterogeneous catalysis, no consensus on the nature of compensation effect has been reached.

2. MATERIALS AND METHODS

Transesterification of croton *megalocarpus* oil was carried out with methanol using alkaline earth catalysts BaO, SrO, CaO, MgO, BeO. Heating was provided by a water bath in studies involving conventional heating, and by a microwave oven in the studies involving microwave irradiation. Mechanical stirring was used to ensure complete mixing, and to eliminate mass transfer resistances. Experimental setup and procedure has been described elsewhere [15]. Croton oil was procured from Help Self-Help Centre, Nairobi. All the reagents were of analytical grade from Sigma Aldrich. GC standards methyl

heptadecanoate, triolein, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were from Sigma Aldrich. Equipment included analytical balance, water bath (Stuart RE 300B, accuracy $\pm 1^\circ\text{C}$), mechanical stirrer (Stuart SS10, 0-2000 rpm), domestic microwave oven (Shivaki, SMW-103, 1300W), voltage regulator, magnetic stirrer (Hanna), thermocouple thermometer (Hanna HI9055), centrifuge (Hettich D-7200), Teflon[®] tubing, standard laboratory glassware. FAME was analyzed using a Gas chromatograph (MRC GC3420A) with flame ionization detector, capillary column Agilent CP-Sil 88 (60m x 0.25mm x 0.36mm, coating 0.2 μm); carrier gas was nitrogen and other gases were hydrogen and air. Gases were of analytical grade. Data analysis was done using Peak-ABC chromatography data handling system. Heating methods were conventional heating in a water bath, and microwave irradiation in a microwave oven. Microwave irradiation is superior to convective heating as it saves substantial reaction time, which in turn is a saving of energy [15], [16].

For kinetics studies, a general rate equation for rate of disappearance of triglyceride, according to overall reaction

$$(i), \text{ was written as, } -r_A = -\frac{d[A]}{dt} = k [A]^m [B]^n \quad \dots(\text{ix})$$

Here A refers to the triglyceride and B refers to methanol. The above equation was integrated for m and n ranging from 0 to 3, for overall reaction order of 'zero' to 'three'. Integrated forms of the equation [17] were used to correlate experimental rate data. Highest correlation coefficient corresponded to the most likely reaction order. Activation energy and pre-exponential factor was obtained by plotting $\ln k$ versus $1/T$ according to equation (vii).

3. RESULTS AND DISCUSSIONS

A total of nine catalyst samples consisting of NaOH, BaO, SrO, CaO, nano CaO, Reoxidized CaO, MgO, nano MgO, and BeO were used for croton oil transesterification. Sodium hydroxide was a homogeneous catalyst used for control purposed. This resulted into eighteen set of data. For the purpose of reporting the catalysts were coded as A (BaO), B (SrO), C (CaO), D (nano-CaO), E (Reoxidized CaO), F (MgO), G (nano MgO), H (BeO) and J (NaOH). Number '1' referred to conventional heating, and '2' used for microwave irradiation. Table 1 gives the observed reaction rate constant (k), Pre-exponential factor A , and Activation energy E for all the nine catalysts, for both conventional and microwave heating.

Table 1: Reaction kinetics parameters k , A and E .

Run	Catalyst	k (at 70°C)	A	E (kJ mol ⁻¹)
1	A1	1.27E-02 (L ² mol ⁻² min ⁻¹)	3.07E+03	35.38
2	B1	6.19E-03 (L ² mol ⁻² min ⁻¹)	7.37E+01	26.61
3	C1	5.65E-03 (L ² mol ⁻² min ⁻¹)	8.80E+02	33.65
4	D1	1.59E-03 (L ² mol ⁻² min ⁻¹)	2.50E+01	27.35
5	E1	9.80E-04 (L ² mol ⁻² min ⁻¹)	2.53E+01	28.74
6	F1	7.20E-04 (L ² mol ⁻² min ⁻¹)	4.18E+00	24.53
7	G1	5.41E-04 (L ² mol ⁻² min ⁻¹)	1.03E+02	34.26
8	H1	8.70E-05 (L ² mol ⁻² min ⁻¹)	7.17E+00	32.05
9	J1	4.75E-01 (L mol ⁻¹ min ⁻¹)	3.73E+10	71.27
10	A2	5.69E-01 (L mol ⁻¹ min ⁻¹)	2.38E+05	36.77
11	B2	4.88E-01 (L mol ⁻¹ min ⁻¹)	5.67E+06	46.2
12	C2	2.68E-01 (L mol ⁻¹ min ⁻¹)	1.79E+03	36.6
13	D2	3.93E-02 (L mol ⁻¹ min ⁻¹)	4.79E+01	20.49
14	E2	3.35E-02 (L mol ⁻¹ min ⁻¹)	2.44E+07	70.3
15	F2	1.62E-03 (min ⁻¹)	7.46E+00	35.58
16	G2	1.53E-03 (min ⁻¹)	2.99E+02	34.7
17	H2	1.52E-03 (min ⁻¹)	7.86E+1	42.33
18	J2	2.45E+00 (min ⁻¹)	2.68E+06	51

Data in Table 1 was used to plot $\ln A$ versus E . Chart 1 gives the resulting Cremer Constable scatter plot.

Solid dots correspond to the data points, and the straight line is a linear correlation line ($R^2 = 0.78$).

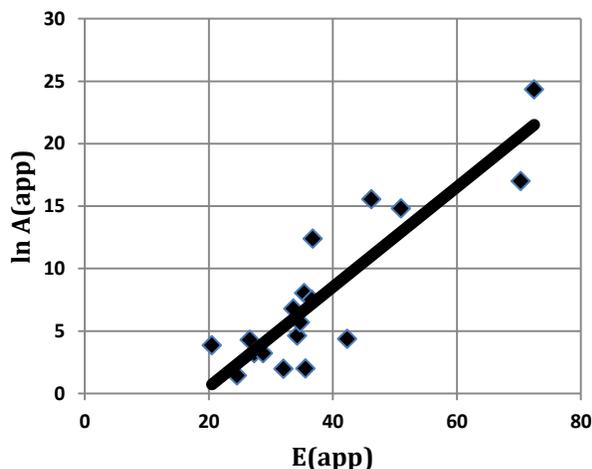


Chart 1: Cremer Constable plot of E^{app} and A_{app} (Eqn viii)

From Table 1, the chemical reaction constant k was highest for NaOH catalyst for both conventional and microwave heating. This means that reaction rates were higher for homogenous catalyst NaOH as compared to alkali metal catalysts. For alkali metals, the highest value of k was for BaO, followed by SrO, Nano CaO, Reoxidized CaO, CaO, Nano MgO, MgO, and BeO. Hence in terms of activity, the catalysts were arranged as: NaOH > BaO > SrO > Nano CaO > Reoxidized CaO > CaO > Nano MgO > MgO > BeO. Similar observations for alkaline earth oxide catalysts have been

reported by other researchers as well [18], [19]. However, no similar trend was noted in pre-exponential factor A and activation energy E . This was suspected to be due to a large number of simultaneous reactions involved in transesterification. Observed values of A and E were therefore ‘apparent’ values for all those reactions. Chart 1 shows that a scatter plot followed a straight line satisfying Cremer Constable equation (viii). The discrepancy was attributed to oversimplification of kinetic analysis. All the reactions were lumped into one expression, equation (ix), resulting into seemingly irrational data. Reaction velocity constant was a multiple of A and $\exp(-E/RT)$, and it was observed (Table 1) that where E values were large, A values were also large, leading to a small value for k . The activation energies for heterogeneous catalysts were not found to be directly related to their activities due to the compensation affect.

4. CONCLUSIONS

Kinetic analysis of transesterification of croton oil with methanol over conventional and microwave heating using homogeneous NaOH and alkali earth metal oxide catalysts gave the highest reaction constant k for NaOH, followed by SrO, Nano CaO, Reoxidized CaO, CaO, Nano MgO, MgO, and BeO. This sequence also gave the order of catalyst activity, highest for NaOH and lowest for BeO. However, no such trend was noted in values of pre-exponential factor A , and activation energy E . It was seen that the magnitude of activation energy was not a direct measure of catalytic activity for heterogeneous catalysts. This was attributed to the compensation effect in heterogeneous catalysis. The overall observed reaction was a result of twenty one or so reaction steps. This complex reaction mechanism resulted into irrational values of A and E . The observed values were thus apparent values, A_{app} and E_{app} , as given in equation (viii). Observed compensation effect was due to data analysis, and not due to a physical phenomena.

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