Research Article

Comparative effect of reaction time on biodiesel production from low free fatty acid beef tallow: a definition of product yield

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Abstract
Review of works in biodiesel production showed that performance of transesterification reaction has always been assessed with wrong notion of product yield. Various researchers defined yield in variety of conflicting ways. This paper addresses the existing confusion in using product yield as reaction performance criterion in biodiesel production. With reference to fundamentals of chemistry and chemical engineering, expression for fatty acid alkyl ester (FAAE) yield in transesterification was derived. The new model was used in comparison with the existing ones, to investigate the effect of transesterification reaction time via homogeneous and heterogeneous base catalyses of beef tallow. Firstly, the physicochemical properties of beef tallow were examined to determine its requirement for esterification pretreatment before the transesterification process. Calcium oxide was derived from eggshell and characterized as catalyst for biodiesel production from beef tallow. Biodiesel was produced at different reaction times and FAAE yield was calculated with all models. By comparison, new yield model gave the least results, with maximum FAAE yields of 94.2% and 87.5% recorded using homogeneous and heterogeneous catalyses respectively. Moreover, heterogeneous catalysis required much reaction time of 4 h to achieve this maximum yield compared to 1 h for homogeneous catalysis. Resolution of some notable limitations of the old models was proved possible using the new one. Yield should be explicitly defined and reported to aid result comparison and design choices in biodiesel production.

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Graphical abstract

$$FAAE\ Yield\ (\%) = \left(\frac{m_{biodiesel}}{m_{lipid}}\right) \times \frac{x_{FAAE}}{x_{TG} \times \left(\frac{3 \times M_{FAAE}}{M_{TG}}\right)} \times 100\ \%$$

Keywords FAAE/FAME yield model · Stoichiometry · Transesterification reaction performance · Biodiesel production · Homogeneous base catalysis · Heterogeneous base catalysis

List of symbols

FAAE	Fatty acid alkyl ester
FAME	Fatty acid methyl ester (simplest and commonest form of FAAE)
FFA	Free fatty acid
TG	Triglyceride (predominant compound contained in most lipids)
x	Mass fraction of species (as indicated with subscript) (wt./wt.)
m	Mass of sample (as indicated with subscript) (g)
M	Average molecular weight of FAAE or TG (as indicated with subscript) (g/mol)
V	Volume of sample (as indicated with subscript) (mL)
ρ	Density of sample (as indicated with subscript) (g/cm^3)
CFPP	Cold filter plugging point
SEM	Scanning electron microscope
XRD	X-ray diffraction
XRF	X-ray flourescence
BET	Brunauer–Emmett–Teller
HPLC	High-performance liquid chromatography
GC	Gas chromatography
MS	Mass spectrometry
AOAC	Association of official analytical chemists
ASTM	American society for testing and materials
JCPDS	Joint committee on powder diffraction standards

1 Introduction

1.1 Brief background to biodiesel production

Biodiesel is a renewable fuel composed of at least 96.5% fatty acid alkyl ester (FAAE) [1], synthesized from lipids of plants, animal or microbial origin [2]. The alkyl end of the FAAE is usually in the range of C_1–C_4 [3], with the commonest being C_1; hence, fatty acid methyl ester (FAME) is most reported. Biodiesel has reduced viscosity than its parent lipid feedstock and is suitable and preferable for use as alternative to (or in blend with) petro-diesel in compression ignition engine without engine modification [4, 5]. Several methods, such as blending of oils, formation of micro-emulsion, thermal cracking (pyrolysis) and transesterification have been employed to reduce the viscosity of lipid biomass but of all, transesterification reaction is the only convenient synthesis route for biodiesel in the laboratory [6] and it involves step-wise substitution of the glycerol (triple hydroxyl functionality) link in triglyceride (TG) molecules of lipids with single short alcohol, usually with methanol, in the presence of acid [7, 8], base, or bio-catalyst [9, 10], or even without catalyst [11]. Figure 1 shows the overall stoichiometric equation for transesterification reaction in structural form. The zigzag structure represents long chain of fatty acid and the colored font is used to illustrate distribution of atoms. From the figure, one mole of TG reacts completely to give 3 mol of FAAE. To favor the forward reaction, suitable alcohol (one with short chain length and single functionality) is added in excess of its stoichiometric requirement.

Fig. 1 Overall stoichiometric equation for transesterification reaction in structural form
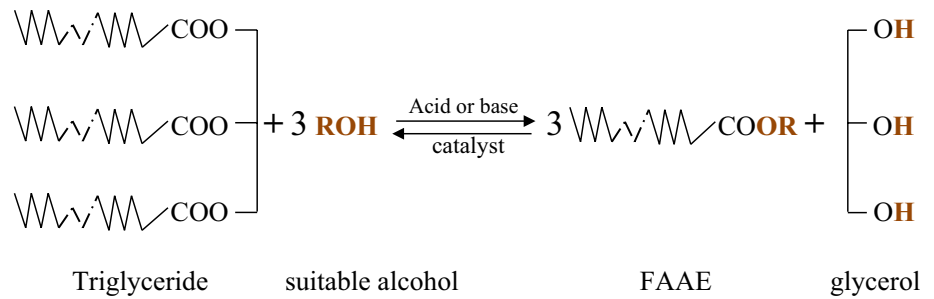
However, transesterification is not as simple as summarized in Fig. 1, it is actually a series reaction for which each step in the series is reversible [8, 12]. The reversible and multiple nature of the reaction reduce the amount of FAAE that can be achieved in reality. Freedman et al. [13] report the variation of transesterification product composition at various reaction conditions; triglycerides, di-glycerides and mono-glycerides were found present with progress of transesterification, in competition with FAAE.

Before going into details of reaction performance, it is noteworthy that the choice of biomass feedstock for biodiesel production is very crucial for process sustainability. Lipids from microbial, inedible and waste resources are recommended to shun food versus fuel competition/crisis [4, 10]. Fats and oil are required for body nourishment; however, saturated fat—usually of animal origin—are required in very limited amount as excess of such nutrients has several health implications [14, 15]. Fats are solid at room temperature while biodiesel from any source should be liquid at ambient temperature, making it easy to distinguish between converted and unconverted feedstock. For this reason, even though animal fat may not be easily sourced in large quantity for commercial sustainable biodiesel production, it is at least beneficial on a laboratory scale.

Furthermore, with the exception of few lipid sources like jojoba (*Simmondsia chinensis*) with unusual oil-wax composition [16], every lipid is an organic mixture comprising of TGs as the predominant component, free fatty acids (FFAs), pigment and other minor compounds, just as biodiesel is composed of FAAE as the predominant compound amongst glycerides and other compounds. But unlike biodiesel, there is no clear cut lower limit of TG composition for lipids [17]. The presence of FFA in lipid feedstock at a level > 1%, calls for acid catalyst treatment step prior to the base catalyzed transesterification, otherwise desired product recovery would be disrupted by undesired product of side-saponification reaction [4, 8, 18].

The two common reactions in biodiesel production, esterification and transesterification are pseudo-homogeneous or heterogeneous fluid–fluid reactions (because two immiscible fluid phases are involved) and according to Levenspiel [19], such reactions are carried out for one of these reasons: to synthesize desired product materials, to facilitate the removal of undesired component from a fluid or to obtain vastly improved product distribution in case of homogeneous multiple reactions. Transesterification is carried out for the first reason; therefore, performance of this reaction should refer to the yield of desired product. On the other hand, esterification matches the second reason; performance should refer to the conversion or consumption of undesired FFA content which serves as the reactant.

1.2 Current measures of reaction performance in biodiesel production

For esterification reaction, performance is judged by the extent of reduction in acid value or FFA content (FFA conversion). However, performance of transesterification reaction in biodiesel production has been reported in variety of ways in literature. Gupta and Agarwal [20] assessed transesterification reaction performance based on percentage yield and defined it as given in Eq. 1, in terms of volume; where: $V_{biodiesel}$ is the volume of recovered biodiesel and V_{lipid} is the volume of lipid used. Use of volume proves controversial because there is no established law of conservation of volume.

$$Yield(\%) = \frac{V_{biodiesel} \times 100}{V_{lipid}} \tag{1}$$

A very similar model but, in terms of mass as given in Eq. 2—where: $m_{biodiesel}$ is the mass of biodiesel and m_{lipid} is the mass of lipid used—is most common [2, 4, 10, 21–23]. By the same analogy, Eq. 3 which has the mass terms of Eq. 2 expressed in terms of volume—but perhaps, intended for molar yield—was used elsewhere [24]; where: ρ and M mean density and average molecular weight respectively, with the subscripts as earlier defined. A stoichiometrically modified form of Eq. 2 (in molar terms) by Cunha et al. [25], which was defined as conversion but discussed as yield, is given in Eq. 4.

$$Yield(\%) = \frac{m_{biodiesel} \times 100}{m_{lipid}} \tag{2}$$

$$Yield(\%) = \frac{V_{biodiesel} \times \rho_{biodiesel} \times M_{FAAE} \times 100}{V_{lipid} \times \rho_{lipid} \times M_{TG}} \qquad (3)$$

$$Conversion(\%) = \frac{m_{biodiesel} \times M_{TG} \times 100}{3 \times m_{lipid} \times M_{FAAE}} \qquad (4)$$

Moreover, some researchers go into detail to account for the actual amount of FAAE in the recovered biodiesel. Equation 5 [5] and Eq. 6 [26] reflect this extension in performance model; where: x_{FAAE} represent the FAAE content (mass fraction). Moradi et al. [27] report performance as expressed in Eq. 5 but they termed it as percentage conversion. Percentage yield is also reported to be equivalent to FAAE content as defined in Eq. 7 [12].

$$Yield(\%) = \frac{x_{FAAE} \times m_{biodiesel} \times 100}{m_{lipid}} \qquad (5)$$

$$Yield(\%) = \frac{x_{FAAE} \times V_{biodiesel} \times 100}{V_{lipid}} \qquad (6)$$

$$Yield(\%) = x_{FAAE} \times 100\% = \frac{mass\ of\ FAAEs\ calculated\ by\ analysis \times 100}{mass\ of\ biodiesel\ phase} \qquad (7)$$

$$Yield(\%) = \frac{V_{biodiesel} \times 100}{theoretical\ volume\ of\ biodiesel\ produced} \qquad (8)$$

Sales [28] reports percentage yield with reference to a theoretical quantity as in Eq. 8, stating that theoretical volume was calculated from molecular weights and densities of lipid and biodiesel; the theoretical volume was not clearly defined. Alptekin et al. [18] report that ester yield is calculated as a ratio of the ester amount to the lipid amount used for transesterification without giving details on how the amounts were calculated. Freedman et al. [13], Ma et al. [29], Demirbas [7] and several other authors also utilized percentage yield as performance criterion but without explicit definition.

$$Purity = x_{FAAE} = \frac{area\ of\ all\ FAAE}{area\ of\ reference} \times \frac{mass\ of\ reference}{mass\ of\ biodiesel\ sample\ used} \qquad (9)$$

Biodiesel purity is expressed by its FAAE content which is usually calculated from gas chromatographic (GC) spectrum. When a reference standard is used in the GC analysis, a more detailed expression for FAAE content (than Eq. 7) is given in Eq. 9 [5, 30–32]. Aghel et al. [31] and Ngamcharussrivichai et al. [12] utilized biodiesel purity as a measure of the transesterification reaction performance.

Now, the limitation of using mere purity as performance criterion is that it does not give any idea to how much of the reaction product can be achieved from a given amount of feedstock. On the other hand, the use of Eqs. 1

or 2 which does not portray product purity at all, is also limited because the claimed biodiesel may not meet the desired composition requirement and therefore may not necessarily be biodiesel. It should be noted that oil is miscible with biodiesel and only purity assessment can reveal the mixture composition. When actually, the extent of conversion is necessary—as in the case of transesterification kinetic studies [4] or development of new synthesis routes [33]—concentration should be ascertained from the reaction mixture, rather than the purified product.

Furthermore, skepticism in sourcing data from literature is bound to exist when terms like yield, conversion and purity are used interchangeably. Veljković et al. [34] compared data from statistical modeling and optimization of biodiesel by ethanolysis, using 'yield (purity)'. Also, in a tabular comparative review of: supercritical, lipase catalyzed and homogeneous catalyzed single step transesterification processes of different waste animal fats by Banković-Ilić et al. [35], the misleading term, "Yield (conversion)" was used to compare transesterification reaction performance from various sources. Perhaps, these are due to the existing confusion in definition of yield for transesterification reaction. Notwithstanding, it is logically wrong to compare values of product yield from different sources with different conflicting definitions (models) of yield. For adequate definition of product yield, we resort to fundamentals of chemical reaction.

1.3 What do chemistry and chemical engineering say about performance of reactions?

With the exception of biochemical reactions which are difficult to predict theoretically, and polymerization reactions where interest lies on product properties, three important commonly used measures of reaction performance are: conversion, selectivity and yield [36]. Conversion is simply the ratio of amount of limiting reactant consumed in the course of reaction, to the initial amount. It is useful in kinetic studies and does not provide any information of reaction product, rather it focuses on reactant. Always, conversion is less than 1 for reversible reactions [19].

When interest is on product, selectivity or yield is used. Selectivity is the fraction of consumed reactant that is transformed to desired product [36–38]. It can also be expressed as ratio of desired to undesired products [19]. This parameter is only useful in multiple reactions [19, 36–38]; otherwise, products (including by-products) of single reactions are always 'desired' (since they result from desired reaction route). Selectivity can take any value from 0 to 1, provided conversion is not zero but it is independent of conversion.

Collectively, product yield accounts for desired product and is affected by: extent of reactant conversion,

undesired side reaction(s) and inefficiency in product recovery or purification. There may be 100% conversion of reactant but if no desired product can be recovered from the process, product yield is zero. Product yield is usually expressed in percentage as shown in Eq. 10.

$$Yield(\%) = \frac{actual\ yeild \times 100}{theoretical\ yield} \qquad (10)$$

where actual yield is the experimentally recovered amount (mass or moles) of desired product, theoretical yield is the ideal maximum amount (at 100% conversion of limiting reactant, 100% selectivity and recovery) of desired product that can be produced as calculated from stoichiometry of balanced chemical equation of the reaction [36, 39–42]. Openstax [40] specifies that yield can be expressed in terms of volume, if the product is a gas. "Yield doesn't mean a thing unless the stoichiometry is right" [43]. Also, Davis and Davis [37] state, "The selectivity and yield should, of course, correctly account for the stoichiometry of the reaction in all cases". It is also worth noting, that yield can never be greater than 100% [40–43].

For better appreciation of the concept of product yield, let us consider an illustrative example by Luberoff [43]. In the manufacture of phthalic anhydride, 100 g of xylene was oxidized to give 103 g of phthalic anhydride. Following the common method in use (Eqs. 1–4, which are based on amount of lipid used), the product yield would be 103% (which is wrong); but from stoichiometric calculation 100 g of xylene would react to give 140 g of phthalic anhydride. Hence, the theoretical yield is 140 g and the percentage yield is 74% [43]. Domingos et al. [44], Kuan et al. [5] and Sales [28] report biodiesel yields in excess of 100%.

Consequently, in the next section, we develop a model for product yield in biodiesel production (transesterification process) and validate the model via experimental study of the effect of transesterification time via homogeneous and heterogeneous catalyses, by comparison of the reviewed existing models and the developed one.

2 Materials and methods

2.1 Derivation of expression for FAAE yield from transesterification process

After transesterification, biodiesel phase is recovered from glycerol (and excess methanol) phase(s) and purified (usually by washing with water and drying). Afterwards, the resulting product which can only be biodiesel if it meets the specification standard [17], is weighed and recorded as mass of recovered biodiesel. The biodiesel should be analyzed for FAAE content (x_{FAAE}) as described by Duvekot

[32]. Actual yield (mass) of FAAE is simply the product of recovered biodiesel mass and its x_{FAAE}. Actual yield in moles can be obtained by dividing the actual mass yield by M_{FAAE}; where M represents average molecular weight, which is obtainable via gas chromatography–mass spectrometry (GC–MS).

Furthermore, we refer to Fig. 1 for stoichiometry, to derive theoretical yield expression using m_{TG} grams of TG; where m_{TG} can be calculated from known mass of lipid sample, if the TG content (x_{TG}) is known ($m_{TG} = m_{lipid} \times x_{TG}$). TG content can be determined according to ASTM D6584 or EN14105 [45]. One mole of TG produces 3 mol of FAAE. Then, m_{TG}/M_{TG} moles of TG would produce $3m_{TG}/M_{TG}$ moles of FAAE. Therefore, the theoretical yield of FAAE is $3m_{TG}/M_{TG}$ moles or $3m_{TG} \times M_{FAAE}/M_{TG}$ grams. Consequently, percentage yield of FAAE is given as expressed in Eq. 11a-c; all the equations are identical therefore anyone can be used.

$$Yield(wt\%) = \frac{actual\ yeild \times 100}{theoretical\ yield} = \frac{m_{biodiesel} \times x_{FAAE}}{3 \times m_{TG} \times M_{FAAE}/M_{TG}} \times 100$$
$$(11a)$$

$$Yield(mol\%) = \frac{actual\ yeild \times 100}{theoretical\ yield} = \frac{(m_{biodiesel} \times x_{FAAE})/M_{FAAE}}{3 \times m_{TG}/M_{TG}} \times 100$$
$$(11b)$$

$$Yield(\%) = \frac{m_{biodiesel} \times x_{FAAE} \times M_{TG}}{3 \times m_{lipid} \times x_{TG} \times M_{FAAE}} \times 100 \qquad (11c)$$

Notice that Eq. 11 reduces to Eq. 5, if and only if $M_{TG} = 3M_{FAAE}$ and TG content is 100%. The former condition arises from stoichiometric consideration and such assumption is unrealistic because the molecular weight of glycerol is less than thrice that of any monohydric alcohol. When the lipid feedstock is assumed to be 100% TG and the biodiesel is 100% FAAE, Eq. 11 reduces to Eq. 4, the 'conversion model' of Cunha et al. [25]. In addition, if the recovered biodiesel is assumed pure (100% FAAE)—another unrealistic assumption due to reversibility of transesterification—the equation further reduces to Eq. 2.

2.2 Preparation and characterization of beef tallow

Three kilograms of freshly cut-out adipose tissue (fat) of cow (*Bos taurus*) was purchased from Fathalla Gomla Market Mall, Borg Al-Arab Alexandria, Egypt. The fresh cow adipose tissues were cut into bits of about 4 cm^3 and the fat content was rendered via dry method by subjecting the cut tissues to heat at 110 °C for 1 h in a pan, to melt the fat and reduce the water content without degrading it. Afterwards, the residual solid was pressed to cake and removed, while the resulting liquid was decanted to remove particulate solids [18, 22]. On cooling, the clear beef tallow was

poured into glass jars, then further cooled to solidification, before the jars were covered air-tight and stored in the refrigerator (at above ice temperature) to reduce chemical degradation due to exposure to atmospheric conditions [46].

Furthermore, samples were taken from one of the tallow jars after melting the content, for characterization. The acid value was determined according to the association of official analytical chemists, AOAC Official Method 940.28 [47]. Saponification value (AOAC Official method 920.160), iodine value (AOAC Official Method 920.159) and moisture content [48], were also determined. The density relative to distilled water was measured using relative density bottle, while the actual density of distilled water was measured with density meter DMA 35 (Anton Paar, Austria) all at 40 °C. The kinematic viscosity at 40 °C was determined according to ASTM D445 using AWD-03 Kinematic Viscosity Tester ASTM D445 (Dalian All World I/E Co. Ltd.) equipped with Pinkevitch Viscometer Glass Capillary Tubes. Melting point, was measured using Digital Melting Point Apparatus by noting the temperature at which solid fat sample enclosed in a slide begins to melt and the temperature when it is completely liquid [48]. The flash point and fire point were determined according to ASTM D92 using GD-3536D Automatic coc Flash Point Tester (Chongqing Gold Ltd, China). The fatty acid composition of beef tallow was determined using Gas Chromatography-Mass Spectrometer, GC–MS (Shimadzu GCMS-QP2010 Ultra) equipped with HP-5MS capillary column of 30 m length by 0.25 mm internal diameter and 0.25 µm film thickness using helium carrier gas via the derivatization to methyl ester method as described by Nollet [49]. Table 1 shows the physicochemical properties of the beef tallow. The tallow had FFA content below 2 mg KOH/g of oil and therefore required no pretreatment by esterification [4].

2.3 Biodiesel production via homogeneous catalyzed methanolysis (transesterification with methanol)

Biodiesel was produced with a 2-neck 250 mL conical flask with minor neck fitted for temperature probe of the magnetic stirrer with the aid of rubber stopper and major neck fitted to Graham condenser; over a magnetic hotplate stirrer (MSH-20D, Daihan Scientific Co. Ltd., Korea) which has adequate temperature, stirring and time control system (as a closed continuously stirred tank batch reactor). Reaction conditions were adapted from Ma et al. [29], Ezekannagha et al. [22] and Banković-Ilić et al. [35]. 100 g of melted beef tallow was weighed into the flask and preheated to 65 °C, while 1 g of KOH (catalyst concentration of 1% by weight of lipid exclusive) was completely dissolved in 22.33 g of methanol (methanol to TG molar ratio of 6:1). Afterwards,

Table 1 Physicochemical properties of beef tallow

Acid value (mg KOH/g)	1.07
Saponification value (mg KOH/g)	191.73
Iodine value (g I_2/100 g)	49.2
Moisture content (wt%)	0.12
Actual density at 40 °C (kg/m^3)	877.98
Kinematic viscosity at 40 °C (mm^2/s)	32.37
Appearance in molten state	brownish-yellow liquid
Melting point (°C)	32–40
Appearance in frozen state	Whitish waxy solid
Flash point (°C)	318
Fire point (°C)	356
Fatty acid profile	(%)
Myristic acid, C14:0	2.19
Palmitic acid, C16:0	28.39
Stearic acid, C18:0	29.81
Oleic acid, C18:1	39.61
Average FFA molecular weight (g/mol)	274
Average TG molecular weight, M_{TG} (g/mol)	860

the catalyst activated methanol mixture was added to the preheated oil and the reactor system was set and run with stirring speed of 1000 rpm and reaction time of 1 min. The schematic diagram of the experimental set-up is shown in Fig. 2. At the end of the reaction time—as notified by Stirrer MSH-20D alarm—the flask was disconnected, and the liquid content was completely and carefully (to minimize losses) poured into a clean, dry and clamped 250 mL separating funnel. The procedure was repeated with reaction times of: 5, 10, 30, 60, 90 and 120 min. The clamped-labeled separating funnels with their content, were left overnight (for about 15 h) for phase separation by gravity settling.

Next, the bottom layer which was identified (by its high density and miscibility with water) as glycerol-rich phase was tapped off and the remaining biodiesel-rich phase was washed gently with warm water till the pH of the waste wash water became the same as that of fresh wash water. The washed samples were carefully transferred into 250 mL beakers and dried in two stages. First, in a humidity chamber HC6-2 (Sheldon Manufacturing Inc., USA), at 90 °C, zero humidity and for 24 h, to gradually remove water which separate, amass and settle on heating the wet organic phase. This step is very important for biodiesel drying by heating; otherwise, the amassed water enclosed by biodiesel phase would bump (with pop sound) due to sudden release from the trap/enclosure when heated above its boiling point. This is hazardous and detrimental to product yield (recovery amount). Secondly, the samples were further dried in GC-4000 Oven (GL Sciences
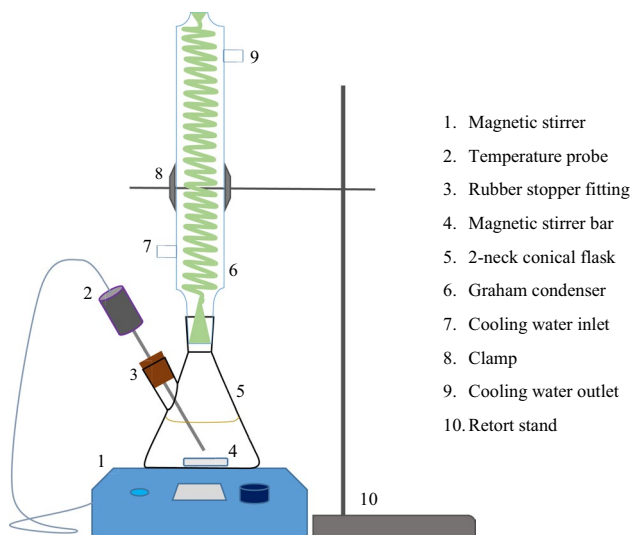
1. Magnetic stirrer
2. Temperature probe
3. Rubber stopper fitting
4. Magnetic stirrer bar
5. 2-neck conical flask
6. Graham condenser
7. Cooling water inlet
8. Clamp
9. Cooling water outlet
10. Retort stand

Fig. 2 Experimental set-up for biodiesel production

Inc., Japan), at 105 °C for 3 h. The dried samples were then weighed ($m_{biodiesel}$) and characterized.

2.4 Preparation and characterization of heterogeneous catalyst

Waste shells of boiled chicken eggs were obtained from Awlad Saad Restaurant, Borg El'Arab Egypt. On arrival to the laboratory, the waste shells were sorted to remove remains of the edible part and any other waste material like vegetables. The shells were soaked and washed severally with distilled water till the wash water became clear. Afterwards, they were drained of water and dried in D-78532 Binder Oven Dryer (Tuttlingen, Germany), for 24 h at 110 °C to ease size reduction. The dried shells were milled with Rose GTM-8302 milling system and sieved. Particles in the size range of 45–63 micron were calcined in muffle furnace KBF794N1 (Koyo Thermo Systems Co. Ltd., Japan), at 900 °C with heating rate of 5 °C/min, for 3 h, cooled in the humidity chamber and stored air-tight in an autoclavable glass bottle [31, 50].

The morphology, BET surface, X-ray diffraction (XRD) pattern and composition of the powdered sample were examined by scanning electron microscopy (SEM) using scanning electron microscope (SEM) (JEOL JSM-6010LV), nitrogen adsorption–desorption using BET surface area analyzer Belsorp II (BEL Japan Inc.), XRD analysis using X-ray diffractometer (Shimadzu Xlab 6100) and XRF analysis with X-ray flourescence spectrometer (Rigaku NEX CGEDXRF), all respectively.

2.5 Biodiesel production via heterogeneous catalyzed methanolysis

Methanolysis of beef tallow in the presence of eggshell derived catalyst was performed at favorable reaction conditions [29, 51] with slight modification to the method earlier described for homogeneous catalysis. First, 8 g of the prepared catalyst (8 wt% concentration by weight of lipid) was weighed into 44.65 g of methanol (12:1 methanol to lipid ratio), covered and mixed in Ultrasonic bath (08895-83 Cole Parmer), for 20 min. Meanwhile, 100 g of beef tallow was preheated to reaction temperature of 65 °C in the 2-neck flask. Afterwards, the methanol-catalyst mixture was emptied into the flask and the reactor was set-up with stirring speed of 1500 rpm and run for reaction time of 10 min. At the end of the reaction, the reactor content was first separated by centrifugation at 6000 rpm using Centrifuge D-78532 (Tuttlingen, Germany) equipped with 8×12 mL glass vial, for 20 min, after which the liquid layer was decanted into separating funnel. The procedure was repeated for reaction times of: 60, 150 and 240 min. Recovery and treatment/washing (in the funnel) and drying of biodiesel were carried out as earlier described. The dried samples were then weighed and characterized.

2.6 Characterization of produced biodiesel

FAME content or purity of each of the biodiesel samples was determined by GC analysis using mass spectrometer (MS) detector [16]. The GCMS-QP2010 Ultra was equipped with DB-5 column (30 m length by 0.25 mm internal diameter, 0.25 μm film thickness) with helium carrier gas. The MS detector was set at ionsource temperature and interface temperature of 250 °C each. Each sample was dissolved in diethyl ether solvent and injected with split injector (ratio of 1:50) at 250 °C with AOC-20i autosampler, alongside GCMSsolution software for data elaboration. The FAME content was calculated as the sum of percentage area of methyl esters of fatty acids in each sample. For the biodiesel sample with maximum yield, the density, viscosity, acid value, iodine value, water content, flash point and fire point were determined as in Sect. 2.2. While the pour point and cloud point were determined according to ASTM D97 and ASTM D2500 respectively, using GD-510D Petroleum Products Pour Points & Cloud Point Tester (Chongqing Gold Ltd, China). Cold filter plugging point (CFPP) was manually determined by filtering sample through 0.45 micron membrane filter, per unit fall in temperature, while cooling was effected using ALPHA RA 8 Chiller (Lauda, Germany) in accordance with ASTM D6371.

3 Results and discussion

3.1 Physicochemical properties of beef tallow

The physicochemical properties of beef tallow given in Table 1, shows a very low FFA content of 1.07 mg KOH/g of oil, because the tallow was rendered from fresh adipose tissues. As expected, the lipid feedstock had very high viscosity and melting point, this discourages direct use in engines at ambient temperature. The flash point and fire point of lipid feedstock are rarely reported and such information may be useful where the lipids are utilized as fuel oils and even for safety in food processing—the case of high temperature frying, etc. High values of 318 and 356 °C were obtained as flash and fire points of the beef tallow respectively. Only four fatty acids were identified by GC–MS with oleic acid being the only unsaturated acid. The ratio of saturated to unsaturated fatty acids is 3:2. These data are slightly different from literature values [52]. However Wood et al. [53] noted several reasons why such variations are bound to occur; such as variation in feeding culture of livestock.

3.2 Characterization of eggshell derived catalyst

After calcination, the initially coarse, milk coloured eggshell particles with characteristic smell became soft, white and odourless [54]. Figure 3a shows the SEM image of the powder derived from chicken eggshells after calcination at 900 °C for 3 h. The material particle size is in the micro scale with honeycomb surface morphology and tortuous porosity. Similar morphology is reported by Niju et al. [50]. Figure 3b shows the XRD spectrum of the powder material with the peaks identified as CaO and $Ca(OH)_2$ by matching with data of joint committee on powder diffraction standards, JCPDS file No. 017-0912 and JCPDS file 84-1264 respectively. The observed hydroxide must have resulted from atmospheric moisture contamination during sampling, according to Eq. 12.

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \tag{12}$$

The XRD pattern shows that CaO is the active material in the catalyst powder and this was confirmed from the XRF data which revealed CaO content of 98.91%, amongst TiO_2 (0.074%), MnO (0.08%), Fe_2O_3 (0.082%) and some trace elements. This implies that the calcination process effectively converted all the calcium carbonates in the raw chicken eggshell to CaO as desired for transesterification catalysis [31]. To further justify the calcination preparation step, the specific surface area of the particles was determined before and after calcination. Of course, catalytic activity
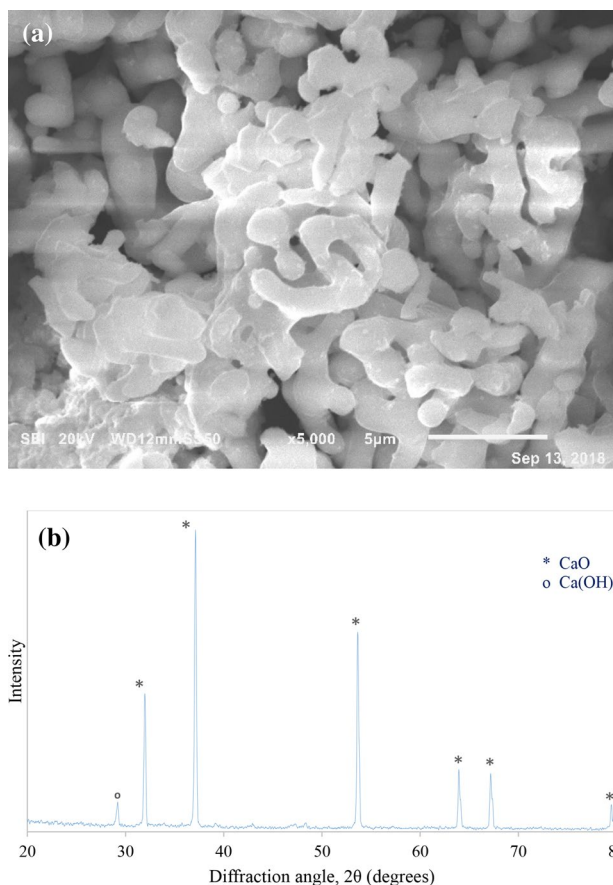
Fig. 3 SEM image (**a**) and XRD Spectrum (**b**) of the powder derived from chicken eggshells after calcination

increases with surface area as more active sites are availed to enhance reaction. The particles had BET surface of 2.98 m^2/g (mean pore diameter of 704.13 nm; total pore volume of 5.53 mm^3/g) before and 3.61 m^2/g (mean pore diameter of 38.17 nm; total pore volume of 35.91 mm^3/g) after calcination. These features are comparable with some earlier works [50, 54].

3.3 Effect of reaction time on beef tallow methanolysis based on various reaction performance models

Methanolysis of beef tallow with either homogeneous or heterogeneous catalyst, resulted in two major experimental data: overall process recovery and FAME content or purity at different reaction times. To a reasonable extent, the two data sets are independent of each other; while recovery is concerned with how much of the hydrophobic (FAME, mono-, di- and tri-glycerides) liquid phase that is obtainable at the end of production, the purity is only concerned with the composition of this recovered phase. The density of each biodiesel sample was also noted and

used for mass-volume conversion. The data were used to calculate FAME yield based on Eqs. 1, 2, 4, 5, 6, 7 and then the developed model, Eq. 11.

First, with KOH as catalyst, Fig. 4 shows the effect of homogeneously catalyzed transesterification reaction time on FAME yield based on different yield models. From the figure, high yield values were attained using Eqs. 1, 2 and 4 (product recovery models) in just 1 min. The yield further increased with time to a certain maximum at reaction time of 10 min before slightly depreciating beyond 1 h. The effect of time using these product recovery models is rarely appreciated because the yield is always high and virtually constant [21–23]. Such high recovery was achieved at the beginning of the reaction due to the high stirrer speed (1000 rpm) used which ensured effective mass transfer between methanol and lipid phases. Once the reaction is well initiated, conversion of TG starts [29] and on separating the mixture at any time, the FAME content should increase with increasing reaction time until equilibrium point is reached, as observed with Eq. 7. Such trends are common in transesterification kinetic studies [4, 55]. However, Eqs. 5, 6 and 11 depend on both overall product recovery as well as FAME content; therefore, they tend to give lower yield values than the rest.

Furthermore, we consider the volume based and mass-based models. Equation 1 is the volume equivalent of Eq. 2, while Eq. 6 is the volume equivalent of Eq. 5. It is obvious from Fig. 4 that the volume-based models resulted to higher values of yield than their mass-based equivalents. As earlier stated, there is no established law of conservation of volume. Such models can only be reasonable when
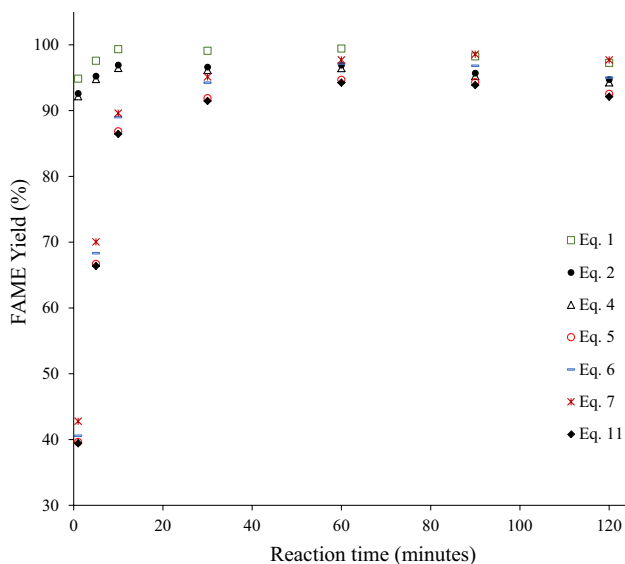
dealing with gases [40]. Use of volume based yield model must have contributed to the unacceptable values of yield (greater than 100%) reported by Sales [28].

In addition, the effect of stoichiometry can be appreciated by comparing Eqs. 2 and 5 with their respective stoichiometrically balanced equivalents (Eqs. 4 and 11). Still from Fig. 4, the values of yield obtained using Eq. 2 is slightly and consistently higher than that using Eq. 4. Also, yield values by Eq. 5 is slightly and consistently higher than that by Eq. 11. This is because, the average molecular weight of TG (860 g/mol) was smaller than thrice that of FAME (864 g/mol). The significance of this would be felt more if ethyl, propyl or butyl alcohol is used. Once again, it is noteworthy that yield is nothing without stoichiometry [43].

On the other hand, for the heterogeneously catalyzed transesterification reaction, poor overall product recovery was achieved in short duration. Figure 5 shows the effect of heterogeneously catalyzed transesterification reaction time on FAME yield based on different yield models. Nothing was recorded for reaction time of 10 min because, after centrifugation of reactor content, very little clear liquid was transferred to the separating funnel and the liquid remained in one phase after about 15 h. The liquid gave cold sensation to touch and mixed well with water—typical of methanol. The solid product of centrifugation was waxy with the catalyst at the bottom. There was no evidence of reaction at this time, so neither recovery nor FAME content was recorded. One notable advantage of using animal fat is its ability to solidify when reactant conversion is insignificant. From Fig. 5, yield generally increased with reaction time for all the models. Compared to yield via homogeneous catalysis, it took longer
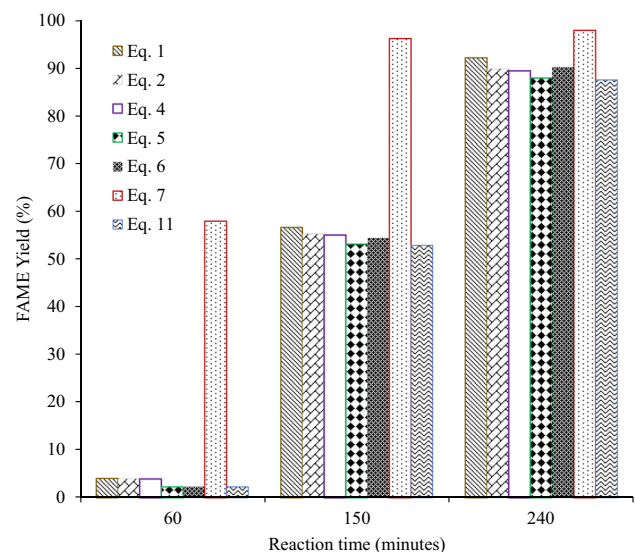

Fig. 4 Effect of homogeneously catalyzed transesterification reaction time on FAME yield based on different yield models

Fig. 5 Effect of heterogeneously catalyzed transesterification reaction time on FAME yield based on different yield models

time to achieve reasonable product yield. This result may be due to the fact that homogenous catalysts are known to be far more active than the heterogeneous ones [51]. Also, mass transfer limitation between the pseudo-homogenous (emulsified) methanol-beef tallow and solid catalyst surface contributes to this time factor. The fact that biodiesel is recovered after additional separation step (centrifugation in this case), reduces the overall recovery. In addition of course, the effects of stoichiometry and using volume rather than mass still apply as earlier discussed for homogeneous catalysis.

Moreover, the new model also accounts for purity of feedstock (x_{TG}). This would be very relevant when dealing with lipids with TG contents well below 100%. Chromatographic analysis for TG is quite different from that for FAME and derivatized fatty acids of lipids [49], and therefore requires another column for GC or other modifications in case of high-performance liquid chromatography (HPLC)—all amounting to extra research cost.

3.4 Properties of beef tallow biodiesel

The biodiesel sample produced in 60 min by homogeneous catalysis which gave a maximum yield of 94% (according to Eq. 11), was assessed for density, viscosity, acid value, iodine value, water content, CFPP, flash point, fire point, pour point and cloud point. Table 2 shows the characteristics of the beef tallow biodiesel alongside European standard. The ester content of 98.56% is satisfactory and the low iodine value is an indication of high level of fatty acid chain unsaturation which is a good indication of fuel chemical stability. For the pour point, on cooling the fuel, flow stopped at 12 °C and according to the test method (ASTM D97), 3 °C was added to this value and that explains why the pour point is reported to be higher than the cloud point (when first trace of waxy crystal was observed). Transesterification successfully reduced the viscosity of the tallow from 32.37 to 6.27 mm²/s. By comparison, the fuel had high viscosity (above recommended limit), but with desirable flash point. It is not suited for cold temperature use due to the relatively high CFPP, cloud and pour points; therefore, blending with petro-diesel is recommendable. However, the properties are comparable to those of Muniyappa et al. [56] and Cunha et al. [25]. The poor cold fuel properties could be due to the high unsaturation of fatty acids [56], evidenced from the low iodine value.

4 Conclusion

This paper dealt with the existing product yield confusion in biodiesel literature. Review of literature for existing measures of the transesterification reaction performance revealed the need to develop an objective model

Table 2 Characteristics of the beef tallow biodiesel

	Results	EN-14214 [1]
Ester content (%)	98.56	≥ 96.5
Acid value (mg KOH/g)	0.48	≤ 0.5
Density at 15 °C (kg/m3)	859.38	860–900
Iodine value (g I_2/100 g)	43.1	≥ 120
Kinematic viscosity at 40 °C (mm²/s)	6.27	3.5–5.0
Water content (mg/kg)	240	≤ 500
CFPP (°C)	12	
Cloud point (°C)	14	
Pour point (°C)	15	
Flash point (°C)	184	> 101
Fire point (°C)	212	

for product yield. Mathematical expression for FAAE yield which considers: the reaction stoichiometry, reactant conversion, TG content of lipid feedstock, product recovery efficiency, and purity of product, was derived for the transesterification process. The effect of reaction time on transesterification reaction performance (yield or what some reports noted as conversion and purity) was reported based on existing models and the newly derived one, revealing the limitations of the existing models. An extension of this study to effects of: catalyst concentration, methanol to lipid ratio, stirring speed and temperature using the respective models, is expected to reveal similar performance trend amongst the models. For clarity, FAAE (compound) yield was used throughout, rather than biodiesel (mixture) yield.

On a final note, if separation of phases is not possible after transesterification, biodiesel yield is automatically zero. The new model addresses the spotted limitations of the existing ones—with the new model, FAAE yield cannot exceed 100%. Whatever the case may be, product yield in biodiesel production should be explicitly defined and reported to aid result comparison and design choices.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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