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Full Length Article

Effect of co-solvent on biodiesel production using calcium aluminium oxide as a reusable catalyst and waste vegetable oil

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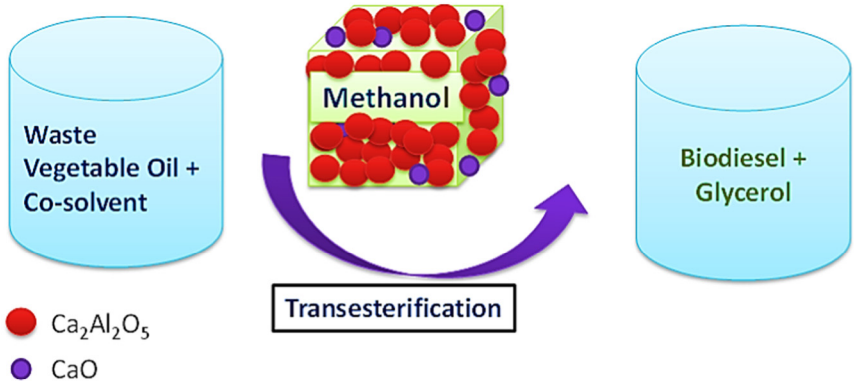
HIGHLIGHTS

- Synthesis of calcium aluminium oxide ($Ca_2Al_2O_5$) carried out by solid state method.
- Calcium aluminate ensued as heterogeneous catalyst for transesterification.
- 97.98% FAME conversion within 25 min attained using acetone as co-solvent.
- Catalyst reused up to 8 runs with >75% conversion in eighth run.

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium aluminium oxide ($Ca_2Al_2O_5$) was synthesized via solid state method by using calcium carbonate and alumina calcined at 900 °C. The synthesized catalyst was characterized by TGA, XRD, FTIR, SEM, and BET. The particle size analysis and basicity test were also conducted. The catalyst was used for production of biodiesel using waste vegetable oil (WVO) as feedstock and methanol through transesterification. Acetone was used and reported as a co-solvent for the first time for synthesis of biodiesel. Effect of co-solvents on reaction parameters has been gaining concern for improvement of transesterification reaction. The reaction parameters such as weight (%) of co-solvent, molar ratio (oil:methanol), catalyst concentration, reaction time, temperature, and reusability of catalyst were studied. Highest conversion (97.98%) of biodiesel was obtained at 20 wt% of acetone, 1:6 M ratio (oil:methanol), 1.2 wt% calcium aluminate at 55 ± 1 °C for 25 min of reaction time. Calcium aluminate could be reused up to eight cycles with >75% FAME conversion at this cycle. Composition of crude WVO and respective FAME was analysed by GCMS technique. Physico-chemical properties of FAME such as acid value, cetane number, calorific value, flash point, fire point, viscosity, density, cloud point, pour point and ash content were evaluated and were found to be within ASTM standards.

1. Introduction

Perpetual demand of fuels worldwide has been increasing tremendously and relies partly on fossil fuels. However, concern about global warming due to carbon emissions from fossil fuel burning has also been increasing [1]. Focussing on this aspect, researchers have derived biofuels such as biodiesel based on renewable resources as a possible substitute for fossil fuels. Biodiesel plays vital role since transportation, agriculture and industrial sectors require huge quantity of diesel, which could be replaced by biodiesel. Biodiesel is non-flammable, non-toxic,

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bio-degradable and has lesser emissions of harmful gases such as sulphur dioxide, carbon monoxide and unburnt hydrocarbons in comparison to petroleum diesel fuel [2].

Among all the methods; transesterification is the best suited method and is mostly used for biodiesel production on commercial scale. It involves 3 mol of alcohol and 1 mol of triglyceride to obtain 3 mol of fatty acid alkyl ester and 1 mol of glycerol. Usually, acid or base catalyst has been utilized in transesterification reaction in which stepwise conversion of triglyceride into diglyceride and mono-glyceride takes place [3]. Transesterification reaction of triglycerides in presence of base catalyst follows SN2 mechanism [4]. Since, oil and alcohol are immiscible, transesterification betide at interface of these two components in heterogeneous system; hence reaction rate and FAME yield are inferior. To overcome this problem, reaction is conducted at boiling point of alcohol in conventional mechanical stirring method to enhance mass transfer between oil and alcohol. It has been anticipated that addition of co-solvents, such as diethyl ether, tetrahydrofuran, acetone or 1,4-dioxane into reaction mixture can increase miscibility of oil in alcohol by forming homogeneous system. Therefore, due to increment in molecule-molecule interaction, reaction can be accomplished in shorter contact time with better FAME yield [5,6].

Acetone is an aprotic solvent, having dipole moment of 2.88 D with intermediate polarity. Hence, it can be properly dissolved both in alcohol (high polarity) and triglycerides (low polarity). Being aprotic solvent, acetone stabilizes active intermediate of transesterification reaction that is methoxide ion as per SN2 mechanism [7]. As a result, acetone has ability to increase the rate of transesterification reaction and hence was considered as a co-solvent for the present work.

Transesterification process can be carried out in presence of homogeneous or heterogeneous catalysts. The major drawbacks of homogeneous catalysts are that they cannot be regenerated since catalyst is used up in the reaction due to which separation is difficult and it needs expensive equipment [8]. To overcome on these demerits of homogeneous catalyst and to diminish environmental along with financial cost of biodiesel production, alternative heterogeneous catalysts have been under consideration in recent years [8]. Heterogeneous catalysts can be easily separated from the product and thus, final product does not contain impurities of the catalyst. Usage of heterogeneous catalyst is environment friendly process since it does not require water in separation and ultimately reduces the cost by regeneration and then regenerated catalyst can be reused as well [9]. This decrement in cost is adequate for biodiesel to compete with fossil diesel. The main characteristics of these catalysts are that they share basic sites on their surface in case of basic transesterification reaction.

Numerous studies have been reported on application of supporting materials such as oxides [10], hydrotalcites [11], zeolites [12], alumina [13,14], silica [13,14], zirconia [13–16], etc. in catalyst synthesis for production of biodiesel in recent years. Zeolites have high surface area, unique pore volume as well as high stability which have attracted researchers' attention in recent years but in microporous materials, mass transfer limitation is a major drawback [17] and with this, the cost of material is also high which makes it unfeasible for biodiesel production. Hence, more efficient, of easier preparation, cheaper and environmentally benign heterogeneous catalyst should be used for large scale biodiesel production. In this perspective, alumina seems to be one of the most appropriate substitute to be used as a support for production of biodiesel. Alumina can be most commonly used as adsorbent, catalyst and catalyst support due to its high specific surface area (above 100 m^2/g). Calcium oxide promoted alumina is eloquently applied as a catalyst in biodiesel production [18–20].

Nayebzadeh et al. [21] have synthesized alumina and calcium aluminate, $CaAl_2O_4$ via microwave combustion method and modified it by potassium hydroxide. This was utilized for transesterification of canola oil with the optimum condition of calcium oxide/alumina molar ratio of 1.48:1, and 23 wt% of potassium hydroxide to CaO-Al_2O_3. The experimental yield obtained was 96.7% (predicted yield 98.3%) at 5 wt% catalyst, 65 °C temperature, 312:1 M ratio of methanol-to-oil for 4 h reaction time. Catalyst sustained its activity up to three runs. Zabeti et al. [20] have reported CaO/Al_2O_3 for transesterification of palm oil. Optimum values of parameters were studied to achieve methyl ester yield of 98.64% at alcohol/oil molar ratio of 12.14:1, catalyst amount of 5.97 wt%, reaction temperature of 64.29 °C and 5 h of time. Benjapornkulaphong et al. [18] utilized $Ca(NO_3)_2/Al_2O_3$ for biodiesel production by using palm kernel oil. In this study, a large amount of methanol/oil molar ratio of 65:1 as well as catalyst amount of 10 wt% was obligatory to achieve 94% methyl ester yield after 3 h of reaction time. In addition to this, considerable reduction in activity of the catalyst was detected when >450 °C of calcination temperature was used for catalyst synthesis, and this restricted its usage at lower temperatures. Ebiura et al. [22] synthesized the catalyst by loading of K_2CO_3 on alumina by impregnation method and used it as a solid base catalyst for transesterification of triolein in presence of methanol and obtained 94% methyl oleate at 333 K in 1 h of reaction time. Lee et al. [23] explored mixed metal oxides (MMOs) activity used as catalyst for biodiesel production. Several MMOs (CaO-MgO, CaO-ZnO, CaO-La_2O_3, and MgO-ZnO) were synthesized through co-precipitation method. Their catalytic activity was improved in the order of, CaO-ZnO (94% ± 1%) > CaO ~ CaO-MgO ~ CaO-La_2O_3 (~90% ± 2%) > MgO-ZnO (83% ± 2%) > MgO (64% ± 1%) > ZnO (41% ± 2%) > La_2O_3 (23% ± 1%). Also, the MMO catalysts, specially CaO-ZnO, showed high reusability in addition to catalyst stability for four cycles in transesterification reaction by using jatropha oil.

However, as per our knowledge, widespread study of calcium aluminate ($Ca_2Al_2O_5$) in the field of biodiesel production by using co-solvent method has not yet been explored. Many researchers have reported that mixture of alumina and calcium oxide could result into various phases of calcium aluminate due to diverse ratios of 'Ca:Al' that affect their acidity and basicity [24–26]. Researchers have applied various techniques of catalyst synthesis and among them co-precipitation, sol-gel, impregnation and hydrothermal methods are often utilized. On the other hand, these methods are costly due to usage of expensive raw materials as well as requirement of several processing steps, hence require longer time making this technique as uncommercial. To synthesize cheap catalyst within shorter span of time, solid state method is the best method which requires small duration and involves low cost, therefore this method was used in the present work.

Feedstock selection for biodiesel production usually depends on its cost and availability. In commercialization of biodiesel production, the major obstruction is the cost of feedstock as it affects up to 70–95% of overall production cost [27]. Due to shortage and high cost of edible oil, usage of these feedstocks was non profitable for large scale production of biodiesel. Hence, the concern was towards non-edible oil usage for biodiesel production [28]. The waste vegetable oil (WVO) was collected from different restaurants and as it was mixture of various vegetable oils, its constituents were determined by using GCMS technique.

In the present work, the catalyst, calcium aluminate ($Ca_2Al_2O_5$) was synthesized by solid state method and characterized by several techniques. The synthesized catalyst was used for biodiesel production from waste vegetable oils in presence of acetone as co-solvent. Optimization parameters such as acetone wt%, molar ratio, catalyst concentration, temperature, time and catalyst reusability were examined. Physicochemical properties of synthesized WVO methyl ester such as acid value, cetane number, calorific value, flash point, fire point, density, viscosity, cloud point, pour