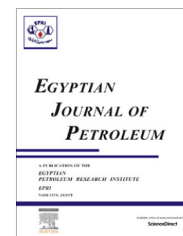




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REVIEW

The study of biodiesel production using CaO as a heterogeneous catalytic reaction

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 Transesterification;
 Heterogeneous catalysis

Abstract With the aim of developing a process of biodiesel production that is environmentally benign much interest has been focused on the use of solid base catalysts, such as calcium oxide, for the transesterification of vegetable oils with methanol. In the study reported herein a recycling reactor was used in bench scale, with the capacity to produce 3 L of biodiesel. The reactor was designed especially for this research study. A full 2^3 factorial plan was used to evaluate the process parameters related to this study, in particular, the catalyst concentration, the alcohol to oil molar ratio and the reaction time. Using this equipment for the transesterification reaction resulted in the recovery of the excess alcohol. The reaction products were characterized using gas chromatography and liquid analysis to determine the ester and calcium concentrations, respectively. The main conclusions drawn were that the best conversion percentage (100% of biodiesel) was reached when the methanol:oil molar ratio was 6:1, the reaction time was 75 min and the catalyst mass was 3% in relation to the oil mass used in this process. The CaO concentration determined exceeded the limit of concentration defined by legislation and thus a secondary operation was carried out to purify the reaction products obtained. The results of this study showed a high performance, and the proposed experiment could be used as a new and innovative way to produce biodiesel in the future.

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1. Introduction

Interest in fuels obtained from renewable sources, such as bio-fuels, has increased significantly in recent years due to the political and economic instability of the oil market, and also because of the environmental benefits associated with decreasing levels of gaseous emissions from the combustion of fuels from non-renewable sources [1–4].

Biodiesel is defined as a non-petroleum fuel produced through a chemical reaction to break down the triglyceride present in fatty acids [5,6]. This reaction is called transesterification or esterification when using as catalyst hydroxides or acids, respectively [7,8]. Biodiesel is a promising alternative to conventional diesel fuel due to its renewable nature and the associated reduction in the emission of particles and greenhouse gases [9–12].

The transesterification reaction is used to break down the chemical structure of the triglycerides in oil via the exchange of the alkyl groups between an ester and an alcohol with the alcohol being used as a reactant. Vegetable oil is subjected to transesterification to decrease the viscosity and increase the volatility of biodiesel [13]. The transesterification process has difficulty converting into esters in the presence of free fatty acids (FFA) and water and, therefore, requires high quality raw materials to avoid undesirable side reactions and hydrolysis (saponification) or additional pre-treatment to remove the initial FFAs [14–16].

The reactions involved in biodiesel production can be homogeneously catalyzed to obtain high yields in a relatively short time; however, biodiesel does not compete favorably with fossil fuels because the catalyst cannot be reused and must be neutralized after the reaction [17]. Environmental concerns have led to the search for solid catalysts which are eco-friendly and effective [18]. The chemical process used to obtain biodiesel is based on the solid in the system catalyzing the reaction to reduce the time and the cost of the process through the reuse of the catalyst, decreasing the level of impurities in the reaction products and carrying out the operation in a continuous fixed bed [19–22].

Studies indicate that the combustion of biodiesel (100%) decreases emissions of greenhouse gases, making it ideal for use in sensitive environments [6,23–25].

The transesterification process efficiency with the use of a heterogeneous catalyst is related to the fact that the catalyst is a solid. Generally, a heterogeneous catalyst provides higher

conversion efficiency than a homogeneous catalyst, and further studies are required to determine the most appropriate time and temperature for each reaction [26].

Recently, research studies have been carried out using calcium oxide (CaO) as a heterogeneous catalyst because of its low production cost [26–30] and its high basicity [28,31].

Liu et al. [32] studied the transesterification of oil using CaO as a heterogeneous catalyst and achieved 95% conversion of the oil to the ester using a methanol to oil molar ratio of 12:01, 8% of CaO in relation to the oil mass and a reaction time of 3 h. Viola et al. [33] performed the same reaction and reached 93% of conversion with 80 min of reaction time using CaO as the catalyst at a reaction temperature of 65 °C using 5% of catalyst in relation to oil (m/m). The authors used a methanol to oil molar ratio of the 6:1. Zhu et al. [34] achieved 93% of conversion using oil from *Jatropha curcas* and a solution of CaO with ammonia carbonate. Watkins et al. [35] carried out a similar study using CaO mixed with lithium as a catalyst. For the biodiesel production in continuum processes, all of the tests by the above-cited authors were conducted in a fixed-bed reactor on laboratory scale, due to the higher production ratio in relation to traditional processes based on bench reactors [36–38].

The results of these studies indicate that the conversion of vegetable oil to biodiesel through transesterification using CaO as a heterogeneous catalyst provides a maximum conversion of 95% in the production of biodiesel when all of the parameters are optimized, mainly the reaction time and molar ratio. These studies were carried out with a bench reactor inside which a mechanical agitator was installed. This equipment can also be used with a solid catalyst. In the literature other similar studies have been reported, where the flow rate of the heterogeneous mixture in the system was determined during the reaction.

In the study reported herein, a commercial oil was used for the transesterification with a heterogeneous catalyst. This paper proposes the innovative use, compared to conventional methods, of a recycling reactor to evaluate a new design for the equipment used in the biodiesel production process. A full 2^3 factorial plan was applied, with a bench reactor and a heterogeneous mixture, to optimize the operating conditions. With respect to the production of biodiesel in this continuous process the conversion was improved, with the possibility of increasing the scale of the process. The ester concentrations were determined by gas chromatography and the CaO concen-

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