Production of environment friendly diesel fuel from sunflower oil over Iraqi limestone synthesized catalyst.

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Abstract. An environment friendly diesel fuel with remarkable characteristics that is basically methyl esters was synthesized from the reaction of sunflower oil (tri-glycerides) with methanol in a batch reactor using a heterogeneous catalyst with a conversion of 94% and very favorable characteristics. The heterogeneous catalyst used in this research was in the form of fine powder and synthesized from Iraqi limestone through calcination at 900 °C for 2.5 h under air. The raw limestone synthesized catalyst was characterized by XRD, SEM, EDX and BET analysis.

1. Introduction

The environmental problems, especially global warming that have been the center of attention recently and have driven many countries to reconsider their energy plans. Thus, procedures and technologies that promote sustainability are nowadays on the top of the list in the field of energy. One of the main activities that resulted in polluting the environment and particularly the atmosphere is the burning of fossil fuel and in order to put this type of pollution at the minimum an alternative to that fuel has to be produced. Thus, along the years researchers have developed several alternatives where biodiesel produced from the transesterification of vegetables oils and animal fats was a very promising one [1]. Greenhouse gases like CO₂ were proven to have a huge impact on climate change thus, legislatures around the world have committed to reducing such emissions via mandates, taxes and subsides; on the other hand, the consumers are applying pressure on industry to limit their impact on the environment [2]. Biodiesel as a fuel derived from renewable resources is basically a mixture of fatty acid alkyl esters that can be produced by the transesterification reaction with glycerol as the byproduct. The transesterification reaction is a reaction between an alcohol- mostly methanol- and glycerides (tri, di and mono), which can be found in vegetable oils and for this reaction to take place at moderate conditions a catalyst will be required, which can be homogeneous or heterogeneous catalysts. The catalysis of the transesterification reaction took a very interesting path, when at some point homogenous catalysts like NaOH and KOH were the most favorable for their reasonable prices and remarkable performance but as the industry of biodiesel grew larger there were several problems that accompanied the use of the homogeneous catalysts in the transesterification reaction like the loss of catalyst and the purification requirement for both products and unreacted alcohol. So, all the attention was shifted toward the heterogeneous catalysts and among them came the calcium oxide as a very promising catalyst to this reaction [3,4]. Calcium oxide as a catalyst can be prepared from a variety of resources, which can be readily found in the nature as in the case of its preparation from limestone and also can be prepared from renewable resources like eggshells and sea creatures’ shells. Basically CaO can be prepared from materials containing calcium carbonate and/or calcium hydroxide by calcination at high temperatures – normally 600-1000 °C for sufficient amount of time that can be up to 3 or even 5 hours in some cases [5]. The use of biodiesel as an alternative to petro-diesel in diesel engines resulted in less emissions of
sulfates, CO$_2$, soot, unburned fuel and lubrication oil (Coordinating Research Council, 1997). The reduction in sulfates emissions that accompanied the use of biodiesel is due to the fact that biodiesel contains no sulfur, in addition there was a significant reduction in the emission of poly aromatics that are considered as toxic compounds [6-9].

2. Materials and Methods

2.1 Materials

Iraqi Limestone, methanol was supplied by Reidel de haen, Germany and sunflower oil was purchased from the local market.

2.2 Methods

2.2.1 Batch production of biodiesel. Biodiesel was produced in a batch reactor (a flask) that was put on hot plate magnetic stirrer. The sunflower oil was added first into the flask and heated up to the desired reaction temperature and then methanol and the catalyst were added to the oil at the desired proportions.

2.2.2 Catalyst preparation. The CaO catalyst was prepared by calcination where the crushed limestone was heated in an electric furnace at 900 °C for about 2.5 h and then the sample was removed from the furnace and stored in a desiccator containing calcium chloride and potassium hydroxide to cool down and then moved to vacuum sterile tubes [10,11].

3. Results and Discussions

3.1 Catalyst characterization

Calcium oxide was characterized by (XRD, SEM, EDX and BET surface area) to get a clear picture on its structural and morphological characteristics, where the XRD test done by the (XRD-6000, Shimadzu, Japan) showed that the resultant material after calcination was CaO and proves that the calcination and the tight storage methods were successful in producing the cheap catalyst from Iraqi limestone and the diffraction pattern can be found in figure (1).

![Figure 1](image.png)

**Figure 1.** Diffraction pattern of CaO

The SEM image observed by the (VEGA 3 LM, Germany) shows that the CaO particles obtained from the calcination are of acceptable shapes and size distribution as can be seen in figure (2), while the EDX analysis presented in figure (3) showed that the ratio of Ca/O is close from the stoichiometric ratio with the presence of a small amount of carbon, which is believed to be adsorbed on the surface of the catalyst later after calcination as the catalyst is very active toward carbon dioxide and moisture present in atmosphere [12].
BET surface area analysis indicated that the surface area of the catalyst was about 3.7202 m$^2$/g, which is a low surface area as compared to other catalysts but an expected one for cases of CaO prepared by calcination at high temperatures as such surface areas are common for such cases.

### 3.2 Transesterification reaction parameters

#### 3.2.1 Mixing intensity

This variable plays an important role in the process of biodiesel production due to the mass transfer limitations caused by the low miscibility between the reaction components (methanol and sunflower oil) [12]. In the case of a heterogeneously catalyzed transesterification reaction a high mixing intensity is a must due to the increased viscosity and density of the mixture and to form a well distributed reaction mixture, especially when relatively high catalyst amounts are used. As can be seen in the figure (4), the best mixing intensity for the present case was 800 rpm and further increasing the intensity had no effect on conversion when using 12:1 methanol to oil molar ratio, 60$^\circ$C.
and 15 %wt catalyst.

![Figure 4. Conversion vs mixing intensity](image1)

**Figure 4.** Conversion vs mixing intensity

### 3.2.2 Methanol to oil molar ratio

This ratio has a tremendous effect on the reaction as it directly affects the reaction reversibility, thus an appropriate ratio will guarantee the shifting of the reaction toward the forward direction resulting in higher conversion and consequently a higher amount of produced biodiesel. From figure (5), it can be seen that the best methanol to oil molar ratio in the present case was 12:1 when the reaction temperature was about 60°C using 15 %wt of CaO and a mixing intensity of about 800 rpm. Increasing this ratio up to 15:1 resulted in lower conversion, which is attributed to a higher external mass transfer resistance caused by the occupation of the basic sites on the surface of the catalyst by the methanol molecules thus, increasing the M:O beyond a certain limit had a negative effect on the conversion [13,14].

![Figure 5. Conversion vs M:O](image2)

**Figure 5.** Conversion vs M:O
3.2.3 Catalyst weight percent. This percentage has a great influence on the transesterification reaction since the reaction was proved in previous researches to be partially governed by mass transfer limitations, especially during the initial part of the reaction due to the adsorption of methanol molecules on the basic active sites of the catalyst. Thus, the amount or percentage of the CaO catalyst was chosen carefully to study its effect on the reaction and consequently on biodiesel production. As can be seen from the figure (6), 15 %wt of the catalyst was the best in the catalysis of the reaction as the conversion obviously increased with the increment of this parameter because of the increased catalyst concentration in the reaction mixture which means that there were more basic active sites available for adsorption and thus the minimization of the mass transfer limitations [10].

![Conversion vs %wt](image)

**Figure 6. Conversion vs %wt**

3.2.4 Effect of temperature. Three different reaction temperatures was investigated in the present case due to the tremendous effect that this parameter has on the transesterification reaction. As can be seen from the figure (7), the conversion was greatly influenced by increasing the temperature from 40 °C to 60°C and this was kind of foreseen since the transesterification reaction is endothermic [15].

![Conversion vs temperature](image)

**Figure 7. Conversion vs temperature**
4. Biodiesel characteristics
The produced biodiesel has undergone several tests to investigate its reliability as a fuel and it was found that its characteristics are within the allowed limits as can be seen in table 1.

Table (1): Biodiesel properties

| Property (units)       | Test result | limits  | reference |
|------------------------|-------------|---------|-----------|
| Acid value (mg KOH/g)  | 0.42        | < 0.8   | ASTM D 664  
|                        |             |         | EN 14104  
|                        |             |         | IRAM 6558  |
| Viscosity (mm²/s)      | 0.49        | 3-6.5   | ASTM D 445  
|                        |             |         | ISO 3104   |
| Density (g/cm³)        | 0.86        | 0.87    | ASTM D 1298/ASTM D 7042  
|                        |             |         | ISO 12185/ISO 3675   |
| Cetane number          | 47          | >47     | ISO 5165   |
| Flashpoint (°C)        | 93          | 100     | ASTM D 613   
| Water content (vol%)   | trace       | <0.08   | ISO 12937   |

5. Conclusions
The tests applied on the material resulted from the calcination prove that calcium oxide can be successfully produced with good characteristics from the Iraqi limestone to be used in the transesterification reaction, where several experiments were carried out to investigate the ability of the produced CaO in the catalysis of the reaction and it was found that the catalytic performance of the CaO produced was good enough to achieve a conversion of about 94 % in 1 hour of reaction time under the previously detailed conditions. Tests carried out on the produced biodiesel and were found to be within the standards thus, the biodiesel produced can be successfully used as a fuel in diesel engines.

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