

Biodiesel: A Cost-effective Fuel Using Waste Materials

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Abstract

The main disadvantage of biodiesel is its high price. The price of biodiesel depends on various factors such as the price of oil, methanol, catalyst, and labor. Among different economic factors, oil accounts for the largest share of input costs of biodiesel production. In this study, first, suitable heterogeneous catalysts were identified for biodiesel production. Several studies were carried out on biodiesel production using heterogeneous catalysts. All of these studies were designed to confirm that the production of biodiesel was cheaper than that of petroleum diesel. Waste materials as feedstock were used for this purpose. In transesterification reaction, waste cooking oil and waste materials were used as catalysts. Alkaline earth metal oxides catalysts are the best kind of heterogeneous catalysts. The catalytic reactivity of alkaline earth metal oxides including waste source of calcium oxide and magnesium oxide, $\text{CaO}/\text{Al}_2\text{O}_3$, CaO/SiO_2 , BaO/SiO_2 , and MgO/SiO_2 were evaluated by the transesterification of oil and methanol. In this study, the costs of produced biodiesel were compared for different sources. The results indicated that the cost of produced biodiesel using synthetic catalysts was 1.26 to 1.49 times that using natural catalysts (1.26 and 1.49 are related to waste cooking oil and refined oil, respectively). Consequently, using waste cooking oils and natural catalysts is recommended for biodiesel production. Also, n-hexane as co-solvent was used to increase the solubility of methanol in oil. In presence of n-hexane, the cost of biodiesel production was approximately reduced by 16%.

Keywords

Basic heterogeneous catalysts;
Biodiesel; Economy;
Waste catalyst;
Waste cooking oil.

1. Introduction

At the present time, in order to make progress in industrial machinery and move countries toward development, it is neces-

sary to make use of fuels. In addition, the economic developments all over the world have increased the need for energy resources; as a result, fossil sources such as petroleum, coal, and natural gas have been utilized as major sources of energy. Nevertheless, the amount of fossil fuel available is limited; accordingly, many researchers have focused on the utilization of alternative fuels that

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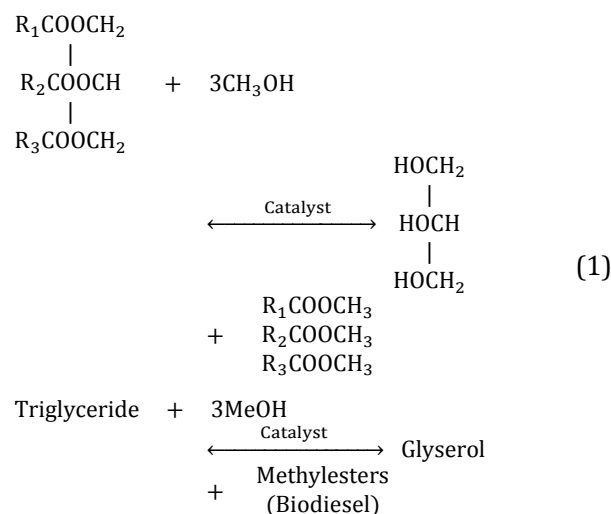
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can be achieved from renewable feedstock. One of the best alternatives among the renewable fuels is biodiesel, which is cleaner than other fuels and is considered to be environmentally friendly. Also, its functional features are almost similar to those of fossil fuels [1-8]. Biodiesel is non-toxic and biodegradable. In addition, it emits low level of pollution and provides better lubricity. As a result, when comparing common diesel fuels with biodiesel, because of its numerous benefits, biodiesel is more favored [9, 10]. Rudolph Diesel was the first person who introduced biodiesel in 1911; he used vegetable oils as an alternative fuel for a diesel engine. Since then, many other people have utilized the idea of using vegetable oils to feed engines [11].

In a technical point of view, biodiesel is a type of fuel that is made of fatty acid methyl ester or mono-alkyl esters, which are themselves extracted from vegetable (plant) oils or animal fats; in addition, biodiesel can be taken from other biomass-derived oils with some specific quality features. In order to chemically convert plant oils into FAMES, it is necessary to carry out a transesterification process.

Transesterification can be performed through a number of methods including acid-catalyzed, alkaline-catalyzed, enzyme catalyzed, or non-catalyzed process. Among the mentioned methods, alkaline catalysts are more frequently used, because this method has a short reaction time as compared with other methods. In order to complete the above-mentioned reaction, normally, it is required to add methanol with a stoichiometric ratio of 3 parts methanol to one part plant oil [12].

While performing a transesterification process, the alcohol used in the process (such as methanol) reacts with the triglyceride oils, which are available in plant oils, animal fats, or recycled greases. As a result of that reaction, fatty acid alkyl esters (biodiesel) and glycerol are produced. In order to successfully complete that reaction, the two factors of heat and strong base catalyst are required. The chemical reaction which occurs during this process is presented below [13]:



Both catalytic and non-catalytic mechanisms can be utilized to carry out a transesterification reaction. In order to perform a non-catalytic transesterification mechanism, supercritical conditions are needed. Because of the specific requirements for supercritical methods, it is necessary to provide higher temperature and pressure; as a result, there is an increase in the parasitic energy required for the process. Therefore, catalytic methods are the most commonly used transesterification methods of biodiesel production, because they require low temperature and pressure [14]. The process of catalytic transesterification can be performed in different forms including homogeneous, heterogeneous, or enzymatic [7, 15].

Recently, there has been an increasing focus on the utilization of solid catalysts for the transesterification process, because the use of heterogeneous catalysts can potentially help to overcome the problems with working with homogeneous catalysts. According to some new studies, the use of a solid base catalyst for the reaction can facilitate the transesterification of vegetable oil with methanol and provide mild reaction conditions [16-26].

Overall, there is an increasing tendency toward the substitution of liquid bases by solid bases, because catalyst separation is energy-intensive and corrosive, and has high costs associated with the disposal of expended or neutralized caustics [27]. Moreover, the use of heterogeneous catalysts for biodiesel production results in a more environmentally friendly process. Furthermore, when solid base catalysts are used for biodiesel produc-

tion, the process is more efficient, continuous, high quality, and cost-effective [28]. Additionally, solid base catalysts can neutralize free fatty acid and prevent production of soaps [29]; as a result, the post-treatment (i.e., separation and purification) processes are more easily performed. Given the numerous advantages of using heterogeneous catalysts in transesterification process for biodiesel production, many studies have increasingly focused on such catalysts over the past ten years. Recent research has also focused on synthesizing novel heterogeneous catalysts with desirable chemical and physical properties for biodiesel production. Nevertheless, it is worth noting that a heterogeneous catalyzed reaction is under the influence of a number of operation variables, feedstock quality, and reactor design [30-35]. Many heterogeneous catalysts, e.g., calcium carbonate, sulfated zirconia, zeolites, alumina loaded with alkaline metal salts, calcium oxide loaded with lithium ion, etc., have been applied for the transesterification reaction in the literature [36-41]. Among the heterogeneous catalysts, calcium oxide has been found as the potential one due to properties such as low cost, low alcohol solubility, high basic strength, non-corrosiveness, environment friendliness, tolerance of moisture, and free fatty acids [42-44]. Calcium oxide can be derived from waste resources, like shells of oysters, chicken egg shells, mud crabs, and waste mollusks [44-48].

One of the main drawbacks of biodiesel is its high cost of production. At present time, the cost of producing biodiesel is about one and a half times the costs of petroleum diesel fuel. As the raw materials and process used for biodiesel production impose high costs, the large-scale production of biodiesel has not been realized yet. Easy access to raw materials can significantly affect biodiesel production process. The availability of raw materials can approximately affect the overall cost of the process by 75-90%. Accordingly, the total cost of the production can be remarkably reduced through finding and using less expensive raw materials. For this reason, it is more cost-effective to take advantage of waste cooking oil, waste frying oils, and animal fats instead of refined vegetable oils. The usual method for transesterification reaction is to use homogeneous catalysts. The application of these catalysts has many drawbacks such as employing significant treatment before water washing and separating the product from homogeneous catalyst, which raise the operating

costs. Homogeneous catalysts are also sensitive to the presence of FFAs and moisture content in oil. Consequently, it is better to use heterogeneous catalysts. Many heterogeneous catalysts have been studied [16, 17, 43, 49, 50]. Research shows that, among the heterogeneous catalysts, solid base catalysts, especially alkaline earth metal oxides, have good performance, since they are inexpensive and have strong basic strength [49, 51, 52].

In this study, it was tried to reduce the costs of biodiesel production. Waste materials as feedstock were used for this purpose. In transesterification reaction, waste cooking oil and waste materials were used as catalysts. The catalytic reactivity of alkaline earth metal oxides, including waste sources of calcium oxide and magnesium oxide, $\text{CaO}/\text{Al}_2\text{O}_3$, CaO/SiO_2 , BaO/SiO_2 , and MgO/SiO_2 , was evaluated by the transesterification of oil and methanol.

2. Methods

2.1. Materials

In this study, waste cooking oil (prepared from local restaurants), methanol 99.5% (Merck), and a heterogeneous catalyst were used for transesterification reaction. Several heterogeneous catalysts such as Mussel shell (collected from Persian Gulf) and demineralized (DM) water plant sedimentation were used as natural catalysts of transesterification reaction.

Also, various synthesized catalysts such as $\text{CaO}/\text{Al}_2\text{O}_3$, CaO/SiO_2 , BaO/SiO_2 , and MgO/SiO_2 were used in transesterification reaction. Deionized water (DIW), nitric acid, aluminum isopropoxide (AIP) (> 98%, Merck), and calcium nitrate tetrahydrate (99%, Merck) were used for $\text{CaO}/\text{Al}_2\text{O}_3$ synthesis. Furthermore, Tetraethyl orthosilicate (TEOS) (>99%, Merck), calcium nitrate tetrahydrate (99%, Merck), deionized water, hydrochloric acid (37%, Merck), and ammonia solution (25%, Merck) were used for CaO/SiO_2 catalyst synthesis. Throughout the synthesis of the catalysts, magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99-102%, Merck) was used as a precursor for magnesium oxide and barium nitrate ($\text{Ba}(\text{NO}_3)_2$, 99%, Merck) was used as a precursor for barium oxide. Also, sulphuric acid (97%, Merck) was applied as the catalyst for esterification reaction.

The reagents used during purification procedure including n-hexane 95% (extra pure, Merck) and methyl laurate (Methyl dodecanoate) $\geq 99.7\%$ were supplied from Sigma as standard for GC analysis and other chemicals were purchased from a local company. Also, potassium hydroxide pellets 85% (GR for analysis, Merck) were used for determination of acidic number.

2.2. Catalysts preparation

In this study, several heterogeneous basic catalysts were used in transesterification reaction. The preparation method and characterization of these natural and synthesis catalysts are explained in this section.

Mussel shell: Mussel shells were milled by mortar and, then, fine particles (125-250 microns) were sieved. The collected particles were calcined inside the furnace at the temperature of 1050°C for 2h [53].

DM water plant sedimentation: DM water plant sedimentation was grinded by a mortar. The obtained powder was sieved to separate micro-particles (125-250 micron) and, then, was dried at 110°C for 18h; afterwards, it was calcined at 900°C in an oven for 2h [54].

CaO/SiO₂, MgO/SiO₂, and BaO/SiO₂: As the first step, a given amount of calcium nitrate tetrahydrate was dissolved in deionized water. Then, hydrochloric acid and TEOS were added to the solution, which was later completely refluxed in 65°C for 2h and 400rpm. Afterwards, ammonium hydroxide was added to the mixture and it was heated at 75°C for 5h. In order to achieve a mixed viscose gel, the surplus water was evaporated gradually. The gel, which was obtained from the previous step, was dried at 110°C for 20h and, then, calcined at 650°C for 3h. In the last stage, the catalyst obtained from the previous steps was crushed and sieved (particles between 125 to 150 microns) and was then used in the biodiesel production process. The same procedure was applied to synthesize MgO/SiO₂ and BaO/SiO₂ catalysts; however, magnesium nitrate hexahydrate and barium nitrate were used as the precursors for MgO and BaO, respectively [55].

CaO/Al₂O₃: In the first step, a given amount of aluminum isopropoxide and HNO₃ were mixed and completely refluxed in 85°C for 1h. In the

next step, calcium nitrate tetrahydrate was added to the mixture and the extra amount of water was evaporated gradually until a mixed gel was obtained. The obtained gel was dried at 120°C for 18h and, then, calcined at 500°C for 6h [56].

2.3. Catalysts characterization

X-ray diffraction (XRD) analysis was used to characterize the crystalline phases of mussel shell, DM water plant sedimentation, CaO/SiO₂, MgO/SiO₂, BaO/SiO₂, and CaO/Al₂O₃ catalysts. Using Cu K α radiation, we performed XRD analysis. Taking into consideration 2-theta in a range of 10-80° with a step of 0.06°, we plotted the intensity (Figs.1-a to 1-f). Moreover, in order to detect elements in the catalysts, we carried out the X-ray fluorescence (XRF) (Spectro Xepor 03 plus) analysis of catalysts (see Table 1).

2.4. The reaction procedure

Esterification reaction: Taking into account the acidic number of waste cooking oil (2 mg KOH/g oil), esterification reaction was done at 65°C for 4h by 5 wt.% of sulphuric acid as catalyst and a mixture of methanol and oil (molar ratio of 6:1) to lower the acidic number to less than 1 mg KOH/ g oil [57]. Thus, the acidic number of waste cooking oil was reduced to 0.49 mg KOH/ g oil.

Table 1. The amount of the main element in the catalysts based on XRF analysis.

| Catalyst type | Element, wt.% | | | | |
|------------------------------------|---------------|-------|-------|-------|-------|
| | Ca | Mg | Ba | Si | Al |
| Mussel shell | 97.77 | - | - | - | - |
| DM water plant sedimentation | 50.58 | 9.34 | - | - | - |
| CaO/SiO ₂ | 40.53 | - | - | 17.54 | - |
| MgO/SiO ₂ | - | 33.84 | - | 17.21 | - |
| BaO/SiO ₂ | - | - | 52.59 | 16.08 | - |
| CaO/Al ₂ O ₃ | 27.22 | - | - | - | 27.74 |

Transesterification reaction: We used different catalysts and waste cooking oil to conduct the transesterification reaction. In order to conduct all the experiments, we used a 250mL two necked flask, which was equipped with a thermometer and a condenser. The mixture of oil, methanol, and catalyst was stirred in 350rpm for 8h and the temperature was kept at 60°C. After the reaction,

centrifugation was performed to separate the catalyst; then, glycerol and the produced biodiesel were separated within a separation funnel. In order to increase the purity, the biodiesel was washed several times by water at a temperature of 90°C. Finally, in order to remove the water, biodiesel was placed in an oven and heated at a temperature of 110°C for 2h.

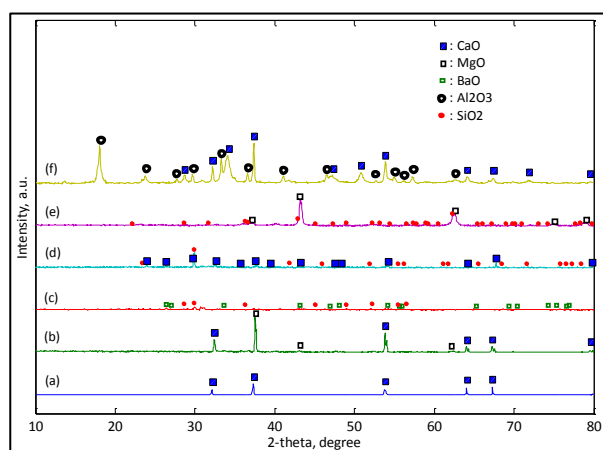


Figure 1. XRD patterns of catalysts; (a) calcined mussel shell at 1050°C for 2h, (b) calcined DM water plant sedimentation at 900°C for 2h, (c) calcined BaO/SiO₂ at 650°C for 3h, (d) calcined CaO/SiO₂ at 650°C for 3h, (e) calcined MgO/SiO₂ at 650°C for 3h, and (f) calcined CaO/Al₂O₃ at 500°C for 6h.

2.5. Product analysis

Gas chromatograph (GC) with a flame ionization detector (FID) was used to characterize fatty acid methyl ester existing in biodiesel samples. The capillary column was a BPX-70 high polar column with a length of 120m, a film thickness of 0.25µm, and an internal diameter of 0.25mm. Nitrogen was used as the carrier gas and as an auxiliary gas for FID. Using a 6890 Agilent Series Injector, 1µL of the sample was injected. The inlet temperature of sample that was entered into the injector was 50°C; it was heated up to 230°C. Methyl laurate (C12:0), as a reference, was added into the crude biodiesel and the samples were analyzed by GC. The weight percentage of FAME or biodiesel purity and conversion were calculated using Eqs. (2) and (3):

$$\text{Purity(\%)} = \frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times 100 \quad (2)$$

$$\text{Conversion(\%)} = \text{Purity} \times \frac{\text{weight of biodiesel produced}}{\text{weight of oil used}} \times 100 \quad (3)$$

2.6. Biodiesel economy

The cost of producing biodiesel fuels depends on various factors including the following: base stock, geographic area, seasonal crop production, the price of crude petroleum, etc. The cost of biodiesel production is normally more than twice the price of petroleum diesel. The high cost of biodiesel is mainly attributed to the high costs of feedstock. Nevertheless, biodiesel can be produced out of other feedstock, including used vegetable oil, beef tallow, pork lard, and yellow grease. Because of its environmental advantages, biodiesel has received more attention recently. The use of cooking oils as a raw material is one of the primary options to reduce the costs of biodiesel production, because it leads to a continuous transesterification process and generates high quality glycerol (a biodiesel byproduct). Because of recent raises in petroleum prices and given the uncertainties concerning petroleum availability, there is an increasing interest in the use of vegetable oil fuels in diesel engines. Currently, the largest part of biodiesels is produced through using soybean oil, methanol, and an alkaline catalyst. Because of the high prices of soybean oil, which is a food product, it is very challenging to produce biodiesel cost effectively. Nevertheless, there are many low-cost oils and fats such as restaurant wastes and animal fats that can be converted to biodiesel. However, processing of these low-cost oils and fats is challenging and problematic, because they often contain large amounts of FFAs that cannot be converted to biodiesel using an alkaline catalyst.

The major economic factor to consider for input costs of biodiesel production is the feedstock, which is about 80% of the total operating cost [58]. Other important costs are related to labor, methanol, and catalyst, which must be added to the feedstock. In this study, the cost of producing biodiesel from various sources is estimated. The cost of biodiesel will be obtained based on anticipated volume and operating expenses. Cost of biodiesel is related to some items that are shown in Table 2. Costs of used materials in this study for biodiesel production are presented in Table 3. Also, density and molar mass of the materials are

shown in this table. These values are used for the mass balance.

3. Results and Discussion

3.1. Catalyst characterization

Fig. 1 showed calcined mussel shell at 1050°C for 2h (Fig. 1-a), calcined DM water plant sedimentation at 900°C for 2h (Fig. 1-b), calcined BaO/SiO₂ at 650°C for 3h (Fig. 1-c), calcined CaO/SiO₂ at 650°C for 3h (Fig. 1-d), calcined MgO/SiO₂ at 650°C for 3h (Fig. 1-e), and calcined CaO/Al₂O₃ at 500°C for 6h (Fig. 1-f), respectively. As illustrated in Fig. 1-a, the calcined mussel shell at 1050 °C consists in CaO. The uncalcined mussel shell consists in a high amount of calcium carbonate [53]. The peaks of Fig. 1-b are related to CaO and MgO. In calcination temperature of 900°C, CaCO₃ and MgCO₃ are converted to CaO and MgO, completely [54]. Also, Figs. 1-c, 1-d, and 1-e showed XRD patterns of 60% CaO/SiO₂, 60% MgO/SiO₂, and 60% BaO/SiO₂ catalysts, which were calcined at 650°C for 3 h. According to these figures, the main diffraction peaks belong to SiO₂, CaO, BaO, and BaO. The peaks in Fig. 1-f relate to Al₂O₃ and CaO. This catalyst contains 40% CaO/Al₂O₃.

3.2. Comparison of different catalysts in the presence of waste cooking oil

As mentioned, approximately 70-95% of the total biodiesel production cost arises from the cost of virgin vegetable oil. The cost of waste oil is very lower than that of refined oil. Thus, the optimal conditions in previous studies [53-56] were re-tested, but waste cooking oil was used instead of refined oil. First, free fatty acid in the waste cooking oil was decreased by esterification reaction. Then, the biodiesel was produced in a transesterification reaction. In this reaction, the mixture of oil, methanol, and catalyst was stirred in 350rpm for 8h and the temperature was kept at 60°C. The conversions of biodiesel in all experiments are presented in Table 4. It is clear that biodiesel conversion at all transesterification reactions is higher than 80%, except in presence of 60% MgO/SiO₂ and 60% BaO/SiO₂ catalysts. These results indicate that the use of waste oil instead of refined oil in biodiesel is not really decreased. However, an esterification step must be performed before the main reaction.

Table 2. Effective items on biodiesel production cost and their descriptions.

| Item | Description |
|-----------------|---|
| Feedstock (Oil) | The cost for accumulating the raw feedstock used to produce biodiesel. If you are personally collecting or growing raw feedstock, this cost may be close to zero. |
| Labor | The hourly wage of the individual that will operate the processor. This cost is about 10\$ per hour for waste cooking oil and 5\$ per hour for refined oil. If you plan to operate the processor yourself, this cost will be zero. |
| Rent/overhead | The cost to rent the land on which your operation will reside. This cost is about 1000\$ per month. If you already own land and have access to water and electricity, or if you plan to offer refining services nomadically, this cost may be negligible. |
| Methanol | Methanol is the recommended alcohol used to create raw biodiesel. |
| Catalyst | The catalyst is acid or base catalyst that is used in the transesterification process. |
| Electricity | The electricity used to operate the processor. Cost of electricity is 0.1\$ per kWh. |
| Sulfuric acid | Sulfuric acid is used in esterification reaction when excessively high amounts of FFAs are present in the raw feedstock. |

Table 3. Cost of materials used in biodiesel production.

| Material | Unit | Cost per unit ^a , \$ | Density, kg.m ⁻³ | Molar mass, g.mol ⁻¹ |
|-------------------------------|------|---------------------------------|-----------------------------|---------------------------------|
| Refined soy-bean oil | L | 0.71 | 882.5 | 863.39 |
| Refined corn oil | L | 0.79 | 879.5 | 859.90 |
| Waste cooking oil | L | 0.11 | 876.5 | 850.11 |
| Methanol | L | 0.53 | 791.8 | 32.04 |
| Sulfuric acid | L | 0.90 | 1840.0 | 98.08 |
| Tetraethyl orthosilicate | L | 9.40 | 940.0 | 208.33 |
| Calcium nitrate tetrahydrate | kg | 5.00 | - | 236.15 |
| Magnesium nitrate hexahydrate | kg | 5.00 | - | 256.41 |
| Barium nitrate | kg | 10.00 | - | 261.34 |
| Aluminum isopropoxide | kg | 13.00 | - | 204.25 |

^a All costs have been extracted from the site www.alibaba.com/products. On this site, global information in materials and their costs exists.

3.3. Biodiesel economy

The utilization of oil and catalyst from waste sources could also counter environmental damage. Consequently, we focused on the exploitation of waste materials as catalysts and waste cooking oil for the production of biodiesel. The costs of

the best synthesized catalysts in this study (CaO/Al₂O₃, CaO/SiO₂, MgO/SiO₂, and BaO/SiO₂) were calculated using their precursors' information. These costs are shown in Table 5. Also, the costs of the other items in biodiesel production were listed in Tables 2 and 3.

Table 4. Comparison of biodiesel conversion using different catalysts in the presence of waste cooking oil at its optimal conditions (stirrer speed of 350rpm, reaction temperature of 60°C, and reaction time of 8h).

| Catalyst type | Calcination temperature, °C | Catalyst concentration, wt.% | Methanol to oil molar ratio | Conversion, % |
|--|-----------------------------|------------------------------|-----------------------------|---------------|
| Mussel shell | 1050, 2h | 12 | 24:1 | 84 |
| DM water plant sedimentation | 900, 2h | 9.08 | 22.49:1 | 83 |
| 40% CaO/Al ₂ O ₃ | 500, 6h | 6 | 12:1 | 83 |
| 60% CaO/SiO ₂ | 650, 3h | 6 | 16:1 | 82 |
| 60% MgO/SiO ₂ | 650, 3h | 6 | 16:1 | 64 |
| 60% BaO/SiO ₂ | 650, 3h | 6 | 16:1 | 60 |
| 70% CaO/SiO ₂ | 650, 3h | 6 | 16:1 | 84 |

A comparative study was carried out about the cost of the produced biodiesel. Using the costs presented in Tables 2, 3, and 5, the cost of the produced biodiesels was calculated from different sources. A process for biodiesel production was considered in a batch reactor with a capacity of 500 gallons (1890L) per batch. The biodiesel cost calculations for different catalysts and oils were performed on this basis (1890L per batch). In addition to reaction time, 2h was considered to fill, empty, and clean the reactors.

Also, 25 days in a month were considered as working days. The information about electricity, dry-wash medium, and other items was extracted from Verde Biofuel site [59]. The price of produced biodiesel using different materials was calculated by production cost calculator. The cost calculation procedure of produced biodiesel from waste cooking oil in the presence of mussel shell catalyst and *n*-hexane at optimum conditions is presented in Table 6.

Table 5. Costs of catalysts used in transesterification reaction.

| Catalyst type | Catalyst loading, wt.% | Cost, \$.kg ⁻¹ |
|------------------------------------|------------------------|---------------------------|
| CaO/Al ₂ O ₃ | 40 | 39.67 |
| CaO/SiO ₂ | 60 | 26.50 |
| BaO/SiO ₂ | 60 | 24.09 |
| MgO/SiO ₂ | 60 | 32.95 |
| CaO/SiO ₂ | 70 | 25.14 |

As shown in this table (Table 6), the cost of producing one liter of biodiesel is equal to 0.33 \$. Through dividing produced biodiesel cost by its conversion, pure biodiesel cost was obtained. Finally, the pure biodiesels costs at various conditions and their conversions are shown in Table 7.

The cost of produced biodiesel using refined oil and synthesized heterogeneous catalysts is more than 1.2\$ per liter [60]. Employing natural catalysts instead of synthetic catalysts reduces the biodiesel production cost to 1\$/L; however, the production cost of biodiesel is higher than that of diesel (the price of diesel is 0.9\$/L) [60]. Thus, in this study, waste cooking oils and waste catalysts were used to produce biodiesel. In this case, the cost of producing one liter of pure biodiesel equals 0.39\$, which is less than half the price of one liter of diesel. Finally, a co-solvent was used to reduce the cost of produced biodiesel. As a result, the cost of producing one liter of pure biodiesel using waste oil, mussel shell catalyst, and *n*-hexane as co-solvent is equal to 0.33\$.

4. Conclusion

Although biodiesel has great advantages compared to diesel, the main disadvantage of biodiesel is its high price. The price of biodiesel depends on various factors such as the price of oil, methanol, catalyst, labor, and other items. The major economic factor to consider for input costs of biodiesel production is the oil. In this study, first, suitable heterogeneous catalysts were identified for biodiesel production. Previous studies have shown that alkaline earth metal oxides catalysts are the best kind of heterogeneous catalysts. Thus, it was tried to find natural catalysts, which were almost free. Mussel shell of Persian Gulf coast and DM water plant sedimentation were used as catalysts for transesterification reaction.

Mussel shell catalysts contained high amounts of CaCO_3 , which were converted to CaO by calcination. The calcium oxide within the catalyst was extracted by methanol during the process. Therefore, the biodiesel conversion was reduced in the catalyst reusability stage [53]. DM water plant sedimentation also contained high amounts of CaCO_3 and MgCO_3 , which were converted to CaO and MgO , respectively, after calcination. This catalyst had high efficiency and only a small amount of calcium oxide was extracted by methanol during catalyst reusing step. Thus, the biodiesel production efficiency by reusing of catalyst did not drop too much. Less extraction rate of CaO from the DM water plant sedimentation catalyst than that from mussel shell catalyst may be due to the presence of MgO in this catalyst [54].

Table 6. Biodiesel cost estimation on the basis of 1890L per batch (biodiesel produced from waste cooking oil in the presence of mussel shell as catalyst and *n*-hexane as co-solvent).

| Item | Unit | Cost per unit, \$ | Units per batch | Cost, \$/batch | Cost, \$/L |
|------------------|-------|-------------------|-----------------|----------------|------------|
| Feedstock (oil) | L | 0.11 | 1890 | 207.90 | 0.11 |
| Labor | h | 10.00 | 7 | 70.00 | 0.04 |
| Rent/ overhead | Month | 1000.00 | 85 | 11.76 | 0.01 |
| Methanol | L | 0.53 | 427.4 | 226.52 | 0.12 |
| Catalyst | kg | 0.00 | 20.02 | 0.00 | 0.00 |
| <i>n</i> -hexane | L | 1.64 | 20.46 | 33.55 | 0.02 |
| Electricity | kWh | 0.10 | 300 | 30.00 | 0.02 |
| Sulfuric acid | L | 0.90 | 49.61 | 44.65 | 0.02 |
| | | | Total cost, \$ | 624.39 | 0.33 |

In order to eliminate or reduce the CaO extraction by methanol, the catalyst was placed on the support. First, CaO was supported on Al_2O_3 by sol-gel and impregnation method; the catalyst reusability, which was supported by sol-gel method, showed a better performance (Biodiesel conversion using sol-gel method after 5 times of reusing catalyst was higher than that obtained by impregnation method, and the CaO extraction rate

from synthesized catalyst by sol-gel method was lower than that from synthesized catalyst by impregnation method) [56]. However, the calcium oxide extraction was high and other supports should be used for this catalyst.

Table 7. Cost and conversion comparison of produced biodiesels from different sources.

| Oil type | Catalyst | Biodiesel conversion, % | Pure biodiesel cost, \$/L | Reference |
|---------------------|--|-------------------------|---------------------------|-----------|
| Refined soybean oil | Mussel shell | 87 | 0.93 | [53] |
| | DM water plant sedimentation | 87 | 0.97 | [54] |
| | 40% $\text{CaO}/\text{Al}_2\text{O}_3$ | 85 | 1.20 | [56] |
| Refined corn oil | 60% CaO/SiO_2 | 82 | 1.25 | [55] |
| | 60% MgO/SiO_2 | 66 | 1.54 | [55] |
| | 60% BaO/SiO_2 | 62 | 1.71 | [55] |
| Waste cooking oil | Mussel shell | 84 | 0.39 | this work |
| | DM water plant sedimentation | 83 | 0.40 | this work |
| | 40% $\text{CaO}/\text{Al}_2\text{O}_3$ | 83 | 0.65 | this work |
| | 60% CaO/SiO_2 | 82 | 0.57 | this work |
| | 60% MgO/SiO_2 | 64 | 0.70 | this work |
| | 60% BaO/SiO_2 | 62 | 0.83 | this work |
| | Mussel shell | 99 | 0.34 | this work |

Then, calcium oxide catalyst was supported on SiO_2 using sol-gel method. The results indicated the high amount of biodiesel conversion. Also, after 5 times of reusing catalyst, a small amount of CaO was extracted and biodiesel conversion fell slightly [55]. The kinetic studies of transesterification [54, 60-62] showed that, at the early stages of the reaction, methanol was not soluble in oil; in addition, reaction was slower in the early stages than in the final moments. The speed of the reaction was determined by diffusion of methanol in oil film and reaction rate on catalyst surface [54, 60-62]. The results of this study showed that a growth in the concentrations of methyl ester and glycerol increased reaction rate constant and the diffusion of methanol molecules in oil film,

which were the resistors in reaction rate determination [54, 60-62]. Therefore, a co-solvent (*n*-hexane) was used to increase the solubility of methanol in oil. This co-solvent reduced the reaction time from 8 to 5h [60]. In addition, the cost of biodiesel production was approximately reduced by 16% (from 0.39\$/L to 0.33\$/L).

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