



Biodiesel Production Using Hybrid Amino Functionalized Chitosan-Carbon Support as Green Catalyst

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PAPER INFO

Paper history:

Received 13 December 2015

Accepted in revised form 03 May 2016

Keywords:

Amino functionalized chitosan

Biodiesel

Transesterification

Base catalyst

ABSTRACT

In this study, Functionalized chitosan with amine groups was synthesized and coated on the surface of carbon black. The hybrid amino functionalized chitosan-carbon support was employed as an efficient, environmentally friendly heterogeneous catalyst for the transesterification reaction of canola oil and methanol. It was observed that this hybrid was more active than parent polymer at the reaction condition. Furthermore, the reaction parameters, such as reaction temperature, molar ratio, amount of the catalyst and reaction time were studied. It was shown that the conversion of canola oil to methyl esters could reach to 95 % during 3.5 h when the reaction was performed with the molar ratio of methanol to canola oil of 12, a catalyst amount of 5 Wt.%, at the reaction temperature of 60 °C. These results can be explained by the inherent basicity of amines groups of amino functionalized chitosan on the surface of carbon support. This novel heterogeneous catalyst offers several attractive advantages such as high catalyst activity, easy recovery and reusability of the catalyst.

1. INTRODUCTION

Fatty acid esters derived from renewable biological sources such as vegetable oils or animal fats have attracted increasing attention in the past two decades due to their lower combustion emission profile (SO₂ and CO₂) and lower pollution emissions. Indeed, numerous studies have shown the benefits of these alternative fuels [1,3].

Biodiesel, which was first tested by Rudolph Diesel in 1900 as a fuel for his engine and was used again during World War II, is now mainly produced by transesterification of oils such as canola, palm, safflower, soybean and sunflower with short-chain alcohols (methanol or ethanol) in the presence of various catalysts including homogeneous and heterogeneous [4,5]. Global biodiesel production is expected to reach 39 billion liter by 2024 corresponding to a 27% increase from 2014 [6]

At present, the biodiesel industry is dominated by application of homogeneous catalysts due to their simple

usage and less time required converting oils to their respective esters. The widely used alkaline catalysts NaOH and KOH are easily soluble in methanol, forming sodium and potassium methoxide and augmenting the reaction to completion [7]. Besides the difficulty of being reused, these homogeneous catalysts have other disadvantages such as equipment corrosion, tedious workup procedure and some environmental problems, but these problems can be avoided by using heterogeneous catalysts [8]. Therefore, it appears of great importance to develop an environmentally friendly solid base catalyst which is able to increase biodiesel yield besides, by its ease of separation and recycling reduces the costs of processing. Some heterogeneous catalysts such as Oxides (CaO, MgO, SrO), Mixed oxides (Mg-Ca oxide, CaO-ZnO), Hydrotalcite and Zeolites have been investigated for the synthesis of biodiesel. Along the last decade, solid catalysts bearing organic groups have demonstrated great potential for various catalyzed organic reactions, among which amine functional groups are well known as base active sites [8,10].

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with regard to the above lines, it has been hypothesized that a heterogeneous catalyst based on an organic polymer bearing basic sites could display good performance in the reaction with biodiesel synthesis. To demonstrate the effectiveness of this synthetic approach in the target reaction, we selected the naturally occurring chitosan biopolymer as a raw substrate to incorporate base functionality and therefore to develop novel bio-organic catalysts. Chitosan, the second most abundant natural bio-polymer, is extracted by deacetylation of chitin, wasted in ton scale in shellfish industries. The interest in chitosan is increasing because of its unique properties (biodegradability, biocompatibility, and low cost polymer) [11,12]. Some research has been undertaken in order to valorize chitosan, and among other options chitosan has found a talented use as a support for catalyst immobilization, with a broad number of applications in different chemical reactions. It could be supposed that the presence of free amino groups and its insolubility in the common organic solvents make chitosan a suitable candidate for solid base catalysts. The evaluation of chitosan as catalyst has been reported rather inadequate, with only some recent successful results in aldol condensation reactions [13]. Apart from the use of chitosan in the aldol condensation reactions, chitosan has hardly been tested for transesterification reaction. For biodiesel synthesis some articles reported catalysts of inorganic oxides (e.g. CaO) or metal ions (e.g. Cu or Co) adsorbed in chitosan [14,15]. Indeed, the transesterification reaction was assumed to be catalyzed by the basic sites such as NH_2 group chemically bonded to the polymer chain even though a fraction of these amine groups are attached to the bulk structure of polymer and they are not accessible to the reagents. It is a fact that the structure of chitosan is unique and some of its physico-chemical properties can be properly tailored by easy chemical modification. Hence, He et al [16] used guanidinylated chitosan (20 Wt. %) for transesterification of soybean oil, a conversion greater than 98% was obtained at 60 °C for 6 h. However, the amino functionalized chitosan with higher accessible amine groups in the surface can be more active than parent biopolymer in the transesterification reaction. On the other hand, the amino functionalized chitosan on the surface of carbon black with high surface area increase the density of accessible basic sites on the surface of catalyst. In this regard, this work was done with the aim of producing biodiesel by transesterification of canola oil and methanol over hybrid amino functionalized chitosan-carbon support as catalyst.

2. EXPERIMENTAL

2.1. Chemicals and Instruments

All the chemicals (AR grade) were commercially available and were purchased from Merck and Aldrich

chemicals. The chemical composition of canola oil and its products obtained in each experiment were analysed using a Chrompack GC Model CP9001 equipped with a Varian capillary column (50 m, 0.25 mm, 0.25 μm) and FID detector. Peaks of methyl esters were identified through comparison with their respective standards.

Also, the acid value and the water content of canola oil were determined according to ASTM D 664 and ASTM D 6304-07, respectively.

2.2. Synthesis of Catalyst

Chitosan derivative (Fig. 1) was prepared following the method proposed by Aghabarari et al [17].

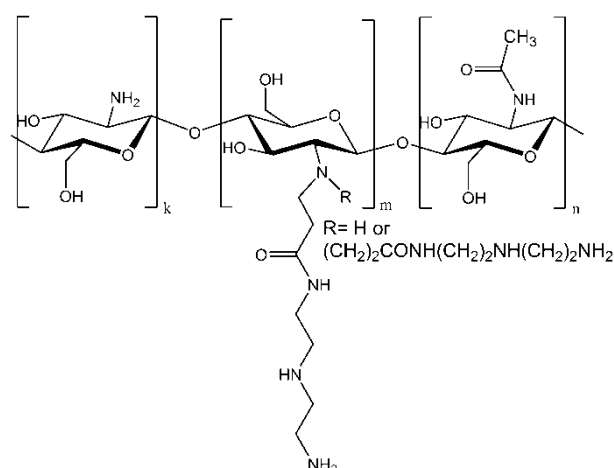


Figure 1. Chitosan derivative

The synthesis procedure includes two steps. *First step:* In a three-neck round bottom flask equipped with condenser, 2 g (12.44 mmol) chitosan in methanol (50 ml, purity, commercial) was stirred at 50 °C for 2 h. To this suspension, a solution of methyl acrylate (49.76 mmol) in 25 ml methanol was added and then the mixture was stirred at the same temperature for 72 h under nitrogen atmosphere. The resultant mixture was cooled and the solid filtered was washed with methanol and dried under vacuum for 12 h. *Second step:* New chitosan derivative was prepared following the same procedure as for *step 1*, but here in this step a solution of diethylene triamine (37.32 mmol) in 25 ml methanol was added to the solid filtered of *step 1* in 50 ml methanol.

The carbon black Vulcan XC 72R (200 mg) was dispersed in 150 ml of 50% isopropanol solution under stirring for 1 hour, then the appropriate amount of chitosan derivative with concentration of 0.5mg/ml in 2 wt.% acetic acid solution was added to the carbon black mixture drop by drop and stirred vigorously for 2 h. Finally the solvent was evaporated by rotary and the sample was dried under reduced pressure at 80 °C for 4 h.

2.3. Chemical Composition of Canola Oil

Biodiesel has different physical and chemical properties compared with diesel fuel and the quality of biodiesel fuel can be influenced by different factors. Accordingly, the properties of the various individual fatty esters that comprise biodiesel determine the biodiesel properties such as cetane number and oxidation stability. On the other hand, the presences of unsaturated fatty acids makes the processing and storage conditions be influenced by chemical composition of oils and fats used in the biodiesel synthesis. For example, the amounts of free fatty acids would remarkably decrease the effect of base catalysts in the biodiesel production process. In the presence of basic catalysts, the free fatty acid contains oil is saponified by homogeneous alkali catalysts, and leads to depletion of the catalysts as well as increment in purification costs [18, 19]. Therefore the chemical composition of the Canola oil was determined using a gas chromatography (GC) and illustrated in Table 1. The molecular weights of Canola oil and biodiesel were 882.32 g and 294.45 g, respectively. Also, the results show that the acid value (0.42 mg KOH g⁻¹) and water content (238 ppm) of the canola oil were low enough for effective base catalyzed transesterification.

TABLE 1. Chemical composition of canola oil.

| Fatty acid * | Composition (wt %) | MW(g.mol ⁻¹) |
|-------------------------|--------------------|--------------------------|
| Palmitic acid (C16:0) | 5.1 | 256.43 |
| Stearic acid (C18:0) | 2.6 | 284.48 |
| Oleic acid (C18:1) | 63.3 | 282.47 |
| Linoleic acid (C18:2) | 19.4 | 280.45 |
| αLinolenic acid (C18:3) | 9.6 | 278.44 |

2.4. General Procedure for Biodiesel Synthesis

The appropriate amounts of Canola oil, methanol and catalyst were added to a 25 cm³, round-bottomed flask fitted with a reflux condenser. The transesterification was typically allowed to proceed for 3 h with vigorous stirring at the desired temperature. After completion of the reaction, the alcohol was distilled off under vacuum, then the residue was centrifuged for 10 min to complete phase separation. Three phases were formed, with the upper layer containing biodiesel, the middle layer glycerol and the lower layer catalyst. After separation, the catalyst was washed with ethanol and dried under vacuum at 70 °C for 4 h. The products were analysed quantitatively by GC using tricaprylin (C₂₇H₅₀O₆, 2,3-di(octanoyloxy)propyl octanoate or Glycerol trioctanoate, MW:470.6823 g/mol, CAS-No. :

538-23-8, EC-No. : 208-686-5) as internal standard. The yield of fatty acid methyl ester was defined as the ratio of the weight of fatty acid methyl esters, as determined by GC, to the weight of fatty acid methyl esters theoretically produced upon transesterification of the oil. Each analysis was carried out three times and data shown were the average values within ±2 % errors.

3. RESULT AND DISCUSSION

3.1. Characterization

Since the hybrid amino functionalized chitosan-carbon support used in this study was obtained by using exactly the same procedure as described in an earlier work, the information on its characterization by FTIR, NMR, CHNS, XPS, TEM and XRD techniques are also collected from the earlier paper [17]. This characterization confirm that chitosan- (N-2 – 2- aminoethylamino ethyl) propanamide) was prepared and supported on carbon black particles successfully. The BET surface area of chitosan, amino functionalized chitosan and hybrid amino functionalized chitosan-carbon support were 2.1, 4.9 and 127.2 m²/g, respectively.

3.2. The Effect of The Different Catalyst and Temperature

The effect of the temperature on the transesterification of canola oil with methanol was investigated in the presence of catalysts (3 Wt.%) including chitosan, amino functionalized chitosan and hybrid amino functionalized chitosan-carbon support in the temperature range 40-80 °C, in steps of 20 °C, methanol to Canola oil (MeOH:oil) molar ratio of 9:1, for 3 h (Table 2).

TABLE 2. The effect of the different catalyst and temperature

| Entry | Catalyst | Temperature (°C) | Yield (%) |
|-------|---|------------------|-----------|
| 1 | Chitosan | 40 | 10 |
| 2 | | 60 | 26 |
| 3 | | 80 | 29 |
| 4 | Amino functionalized chitosan | 40 | 25 |
| 5 | | 60 | 51 |
| 6 | | 80 | 50 |
| 7 | Hybrid amino functionalized chitosan-carbon support | 40 | 33 |
| 8 | | 60 | 59 |
| 9 | | 80 | 59 |

Each analysis was carried out three times and data shown were the average values within $\pm 2\%$ errors. The conversion of fatty acid methyl esters (FAMES) was found to increase with temperature from 40 to 60 °C, although further temperature increases had no significant effect on the conversion in any catalytic system because the evaporation of methanol and as a result, the formation of methanol gas bubble, held back the contact among

methanol, oil and catalytic system.

The results showed that transesterification reaction of canola oil and methanol over amino functionalized chitosan improves the reaction conversion as compared with the parent chitosan. Furthermore, the transesterification reaction showed a better conversion with hybrid amino functionalized chitosan-carbon support as the catalyst.

Regarding the catalytic reaction mechanism in the transesterification, the active sites on the solid base catalysts interact with H^+ from hydroxyl group in methanol molecules to form methoxide ion. Then, carbonyl carbon in a molecule of triglyceride is attacked by a formed methoxide ion to produce bio-diesel. The large size of the triglyceride molecule should result the reaction taken place on the external surface of the catalyst.

Two main factors, namely the number of accessible basic sites on the surface, and the mass transfer rate to these sites, are likely to have a major influence on the transesterification of vegetable oils with base catalysts [10,20]. The more accessible amino groups on the surface of chitosan derivative showed the higher catalytic activity than parent polymer whereas some part of amino groups being in bulk and cannot be act as well as amine groups in new amino functionalized chitosan.

From this view point, when the amino functionalized chitosan supported on the surface of carbon black, the surface area of catalyst increase remarkably and higher number of triglyceride molecules can access to the base active site at the same time. However, hybrid amino functionalized chitosan-carbon support was selected as best catalyst for optimization of reaction condition.

3.3. The Effect of Molar Ratio

The complete transesterification of a triglyceride demands 3 equivalents of methanol, stoichiometrically. Clearly, a number of intermediates like diglycerides will be formed during the biodiesel synthesis. Therefore, to trigger the reaction to a selective fatty acid methyl ester formation, a large excess of alcohol is typically loaded in the reaction mixture. Apart from thermodynamic reasons, an excess of alcohol also enables better rheological conditions for the reaction by reduction of reaction viscosities and restrictive mass transfer limitations.

Based on the average molecular weight of canola oil (882.32 g/mol), the effect of the CH_3OH :Canola oil molar ratio on the transesterification reaction was studied in the

range 3:1 to 15:1 with hybrid amino functionalized chitosan-carbon support as catalyst. The reaction was carried out at 60 °C for a period of 3 h. As shown in Fig. 2 the methyl ester conversion improved considerably upon increasing the methanol to Canola oil (MeOH:oil) molar ratio from 3:1 to 12:1.

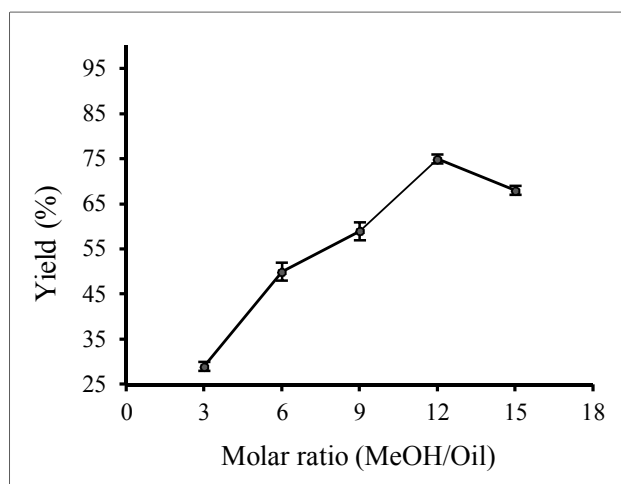


Figure 2. The effect of molar ratio

Since the reactions involved in biodiesel production are reversible, one would expect that increasing the amount of methanol would shift the reaction equilibrium toward the products. Further increase in the molar ratio had little effect, probably as a result of reverse transesterification between the methyl ester and glycerol [21].

3.4. The Effect of Amount of Catalyst

The yield of the reaction is increased upon increasing the amount of catalyst from 1 to 5 wt. %, although further increases have little effect on the conversion (Table 3). An increase in the amount of catalyst to 5 wt. % clearly increases the number of base sites available, although subsequent increases can be reacted with glycerol product and formation of glyceroxide ion with less activity than methoxide doesn't improve the conversion of reaction and biodiesel production [20]. The optimal amount of catalyst was therefore taken to be 5 wt. %.

TABLE 3. The effect of amount of catalyst

| Entry | Amount of catalyst (wt.%) | Yield (%) |
|-------|---------------------------|-----------|
| 1 | - | 36 |
| 2 | 1 | 50 |
| 3 | 3 | 75 |
| 4 | 5 | 89 |
| 5 | 7 | 84 |

3.5. The Effect of Reaction Time

The effect of the reaction time on the transesterification of canola oil was determined using 5wt. % of hybrid amino functionalized chitosan-carbon support, a methanol: oil molar ratio of 12 and a temperature of 60 °C.

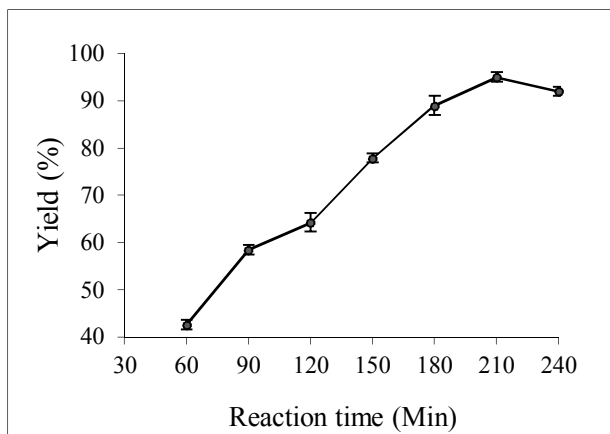


Figure 3. The Effect of reaction time

Fig. 3 shows that the conversion increased from 42% to about 95% after 3.5 h, with little change after this time. This observation can be explained by the fact that the transesterification of vegetable oil is a reversible reaction with an equilibrium time of around 3.5 h, which was therefore taken as the ideal time for the transesterification of canola oil with methanol.

3.6. Reusability

The catalytic stability of hybrid amino functionalized chitosan-carbon support was investigated by performing several runs under the optimised reaction conditions determined above.

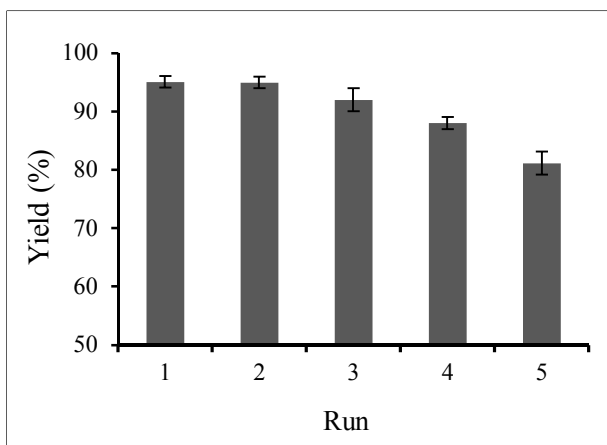


Figure 4. Catalyst recycling of transesterification of canola oil with methanol

The catalyst was separated, washed and dried as described in the experimental section after each run. The recyclability data for this catalyst (Fig. 4) shows that the conversion decreased from 95 to 81 % after fifth runs, thereby confirming the stability of hybrid amino functionalized chitosan-carbon support during the transesterification of canola oil with methanol.

4. CONCLUSION

Chitosan, which is an abundant biopolymer, is a readily available and non-hazardous material, and is usually discarded as a waste material. We have synthesised hybrid amino functionalized chitosan-carbon support which has shown good catalytic performance and reusability for the transesterification of canola oil with methanol.

The transesterification mainly took place on the surface of the catalytic system and the functionalized biopolymer chitosan provided an efficient and sustainable surface amine groups associated with the superior performance of the catalysts.

A conversion of more than 95% has been obtained for the transesterification of canola oil with methanol upon varying several reaction parameters, including temperature, molar ratio, amount of catalyst and reaction time. Encouraged by the observed capability of biopolymer chitosan acting as catalyst for transesterification reactions, the focus was put on another biopolymers, which is also widely available worldwide from bio-resources.

5. ACKNOWLEDGMENT

Support of the Materials and Energy Research Center for this research work to be mentioned with gratitude.

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