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RADIATION GRAFTED NATURAL FIBRES FUNCTIONALIZED WITH ALKALISED AMINE FOR TRANSESTERIFICATION OF COTTONSEED OIL TO BIODIESEL

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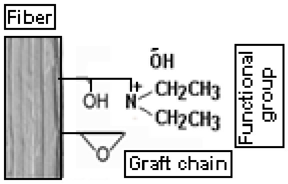
Graphical Abstract



Radiation grafted and aminated catalyst

Abstract

Poly(glycidyl methacrylate) grafted Linum usitatissimum (flax) fibers functionalized with diethylamine (DEA) groups followed by alkalisation were prepared and used as a heterogeneous catalyst for production of biodiesel. Particularly, the new basic catalyst was used for transesterification of cottonseed oil using different molar ratios with methanol and various reaction temperatures. The gas chromatography analysis was used to confirm the conversion of the cottonseed oil to biodiesel. The transesterification reaction temperature affected the conversion percentage significantly. The highest conversion was obtained at 60 °C. In addition, the oil/methanol ratio in the reaction mixture of 1:33 resulted in the highest conversion ratio reaching about 97 %. These results suggest that the alkaline organic catalyst prepared in this study has a potential for application in biodiesel production.

Keywords: Radiation induced grafting, flax fibres, glycidylmethacrylate, heterogeneous catalyst, conttonseed oil, biodiesel

Abstrak

Gentian inum usitatissimum (flax) yang digrafkan dengan poly(glycidyl methacrylate) dan kemudiannya diubah suai dengan diethylamine (DEA) yang seterusnya dialkalikan telah disediakan dan diguna pakai sebagai pemangkin heterogen bagi tujuan penghasilan biodiesel. Pemangkin tersebut digunakan terutamanya bagi proses transesterifikasi minyak biji kapas pada nisbah molar methanol dan suhu tindak balas yang berlainan. Analisis kromatografi gas telah digunakan untuk mengesahkan penukaran minyak kapas kepada biodiesel. Suhu tindak balas transesterifikasi didapati mempengaruhi peratusan penukaran dengan ketara. Penukaran tertinggi diperolehi pada 60 ° C. Di samping itu, nisbah minyak / metanol 1:33 dalam campuran tindak balas memberi nilai penukaran yang tertinggi berjumlah 97 %. Keputusan ini menunjukkan bahawa pemangkin organik alkali yang disediakan mempunyai potensi untuk aplikasi pengeluaran biodiesel.

Kata Kunci: Pengrafan pendorong radiasi, gentian *flax*, glycidylmethacrylate, Pemangkin heterogen, minyak biji kapas, biodiesel

1.0 INTRODUCTION

Today's energy crisis is increasing every day because of the quick growth of population and urbanization. Petroleum-based fuels play a vital role in the global energy demand, which can be used for running vehicles, power plants, and motor engines in the transportation and industrial sectors. However, the unsustainability and the negative environmental impact represented by green gas emission and climate change are the main problems associated with the use of petroleum-based fuels. Therefore, the search for alternative fuels has gained a significant attention. Renewable energy sources such as solar, biomass, geothermal, and wind are one of the best alternatives to meet the escalating global energy demand[1] Nevertheless, most of these alternative energies have low efficiency and only capable of generating thermal and electrical energy, while more than 40% of global demand for energy is in a liquid form. Therefore, the use of biomass has attracted much attention as a new source of alternative liquid fuels such as biodiesel, recently[2]

Biodiesel is a mono alkyl ester of fatty acids produced from vegetable oils or animal fats. In other words, when a vegetable oil or animal fat chemically reacts with an alcohol, it can produce biodiesel, a fuel that can be used in diesel engines after some adjustments and modifications. Vegetable oils contain saturated hydrocarbons (triglycerides), which consist of glycerol and esters of fatty acids[3]. In addition, fatty acids have different numbers of bonds and carbon chain lengths.

Biodiesel production can be carried out by transesterification and/or esterification of triglycerides with alcohols with different types of catalysts. They include homogeneous catalysts (alkaline or acid), heterogeneous catalysts (metal oxide, zeolites, carbonates, heteropolyacids, functionalized zirconia or silica, hydrotalcites, alkaline salts and ion-exchange resins) and biocatalysts (lipase enzyme). Biodiesel can be also produced by non-catalytic supercritical methods.[4, 5]

Currently an alkali catalyst method using homogeneous catalysts such as NaOH, KOH and their alkoxides are commonly used for transesterification of vegetable oils, which is faster in reaction than acidic counterparts. However, a large amount of water is required to transfer the catalysts from the organic phase to a water phase after the reaction. Therefore, it is considerably costly to separate the catalyst from the produced biodiesel.[5-6] Alternatively, ion-exchange resins can be used as a catalyst to solve or minimise this problem with faster reaction kinetics.[4] However, the use of ion exchange resin for this application has not received sufficient attention and their uses remain confined to dehydration of biodiesel. Recently, grafted polymer fibres are proposed as a solid basic catalyst for transesterification of vegetable oil.[7] This was motivated by the successful modification of polymer fibres by radiation-induced grafting that could impart desired functional groups enabling them to be used as adsorbents for chemical water treatment.[8-9] Recently, Ueki et al reported the use of the poly(glycidyl methacrylate) grafted nonwoven polyethylene fabric for preparation of a basic catalyst that tested for transesterification of triolin into biodiesel.[10]

In present study, a new alkaline catalyst is prepared based Linum usitatissimum (flax) fibres which were used as a substrate to prepare basic catalyst by radiation induced grafting of glycidylmethacrylate (GMA) and subsequent chemical treatments with diethylamine and NaOH solutions. The obtained functionalized fibrous catalyst was tested for transesterification of cottonseed oil with methanol. The effect of reaction parameters such as cottonseed oil/methanol molar ratio and reaction time on biodiesel conversion is investigated and the preliminary results are reported.

2.0 METHODOLOGY

2.1 Materials

Flax was obtained from Tanta Flax Ltd Co. (Egypt). GMA of 97% purity, polyoxyethylenesorbitan monolaurate (Tween-20) and isopropanol, were purchased from Sigma Aldrich and used without further purification. 97% Sodium hydroxide, 80% Sodium chlorite and ≥65% nitric acid (Sigma Aldrich) were used to prepare solutions in double distilled water with desired concentrations. The cottonseed oil was obtained from a commercial source in Sudan. Diethylamine (DEA, 99.5% purity), methanol (99.8%) were purchased from Segma Aldrich. All chemicals were used without further purification.

2.2 Procedure

Grafted and functionalized flax fibrous catalyst was prepared by pre-irradiation of the fibres with electron beam accelerator followed by emulsion graft polymerization of GMA onto the irradiated fibres as described elsewhere.[11] The grafted fibres were functionalized by treatment with diethylamine (DEA) and NaOH solution. The performance of the functionalized fibrous catalyst was evaluated for the transesterification of the triglyceride in the cottonseed oil and methanol in a batch mode. A 3-necked glass flask was initially filled with 20 ml of cottonseed oil and a desired amount of methanol and mixed for 10 minutes. A 0.1 g of the aminated and alkalised grafted fibbers catalyst was added to the reaction solution, and the mixture was heated while stirring at 400 rpm using a motorized stirrer. The reaction was allowed for 1 h in all experiments. Since the transesterification of triglycerides can produce methyl ester (biodiesel) and by-product, glycerol. Hence, the conversion of oil was calculated based on the amount of recovered glycerol according to the following equation:

Conversion (%) = (Mole of experimental glycerol/Mole of theoretical glycerol) x 100 (1)

2.3 Characterization of Alkaline Catalyst

SEM images of the fibres samples were obtained using a FEI Quanta 4000 scanning electron microscope.

FT-IR analysis was conducted using a Perkin Elmer Spectrum One FT-IR spectrometer.

3.0 RESULTS AND DISCUSSION

Fibrous catalyst for biodiesel production was prepared with radiation induced grafting of GMA onto flax fibres, followed by amination and alkalisation reactions. The degree of grafting on the grafted fibres was 147%. The amine conversion of incorporated epoxy group on grafted fibres was 84.2% using DEA in H_2O, 50/50 mixture at 70°C for 1 h.

3.1 Morphological Properties

The SEM was recorded to determine the morphology and changes in fibre size of prepared catalyst. The morphologies of raw flax, bleached, grafted and aminated flax fibres are presented in Figure 1. It can be seen that the surface morphology of fibres changed after each reaction. For instance, the bleached flax fibre showed smooth cylindrical rod like with clean microfibrils structure compared to the rough surface with a network structure depicted in the pristine flax fibre. The grafted flax fibres is thickened by the grafted poly(GMA), which subsequently swollen when treated with DEA causing the microfibrils structure to purse. These results provide evidence for grafting and amination.

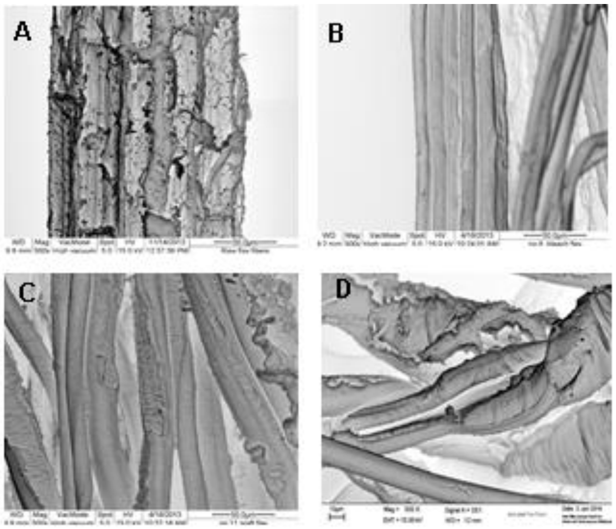


Figure 1 SEM images of (A) raw flax fibres (B) bleached flax fibres (c) grafted flax fibres and (D) aminated flax fibres.

3.2 Chemical Analysis

FTIR spectra of raw, bleached, grafted and aminated flax fibres are shown in Figure 2. The lignin characteristic peaks at 1603 and 778 cm^{-1} in the pristine flax fibre were reduced in size after bleaching. The epoxy group characteristic peaks at 1253, 903 and 842 cm^{-1} appeared after GMA grafting. The introduction of DEA imparted a broad peak at 3328 cm^{-1} resembling–NH_2 overlapping with that of -OH at 3282 cm^{-1} in grafted fibre. This was coupled with sever reduction in the absorption peaks of the epoxy rings revealing that majority of them were opened by the addition of DEA. Hence, it can be confirmed that amine containing catalyst was successfully obtained by radiation induced grafting of poly(GMA) and subsequent amination. Table 1 shows the properties of the aminated fibrous catalyst.

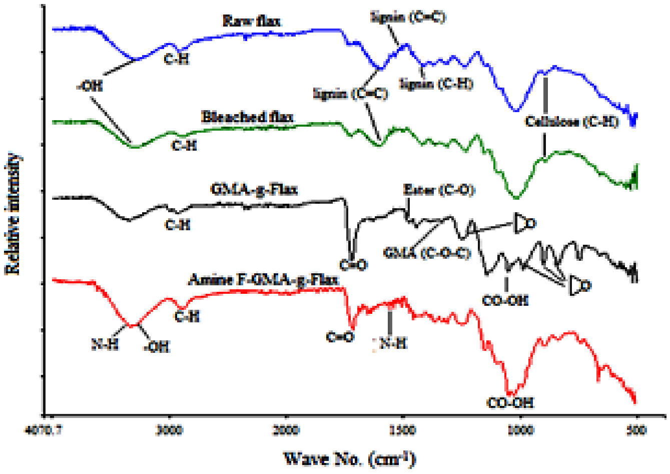


Figure 2 FTIR spectra of raw flax fibres, bleached flax fibres, grafted flax fibres and aminated flax fibres.

Table 1 Properties of grafted fibrous catalyst

Properties	Values
Degree of grafting (%)	147%
Function group	Amine/OH(-NH$^+$/OH$^-$)
Amine group density	3.5 mmol/g

The effect of the transesterification reaction parameters namely temperature and oil/methanol molar ratios were investigated. Other reaction parameters were maintained and constant values.

3.3 Effect of the Reaction Temperature

To examine the effect of the reaction parameters on transesterification reaction, amine functionalised catalyst with the properties shown in Table 1 was used. The effect of the reaction temperature on the biodiesel conversion during transesterification of cotton seed oil is shown in Figure 3. The molar ratio of cottonseed oil to methanol was 1:33. It was observed that the conversion of cottonseed oil increased with the increase in the the reaction temperature until the temperature of 60°C beyond which it started to decline with the rise in temperature. The highest conversion of cottonseed oil was 97%, which was obtained at 60 °C and dropped to 92% and 75% at 65 °C and 70 °C, respectively. This trend is due to the increase in the catalytic activity with the temperature rise up to 60°C, beyond which the methanol tends to evaporate and remains in the vapour phase in the reaction vessel. Hence, the methanol was reduced in the reaction medium and as a result, the conversion was decreased. Similar increase in biodiesel conversion during other transesterification reactions with the temperature rise using anion exchange catalysts was reported reported in literature.[12-14]

3.4 Effect of Cottonseed Oil/Methanol Molar Ratio

The effect of the molar ratio of cottonseed oil to methanol in the reaction mixture on the conversion during transesterification reaction was investigated and the results are shown in Figure 4. The molar ratios of cottonseed oil to methanol were varied according to ratios: 1:3, 1:12, 1:33, 1:100, 1:200, and 1:500.

The molar ratio of cottonseed oil to methanol showed a significant effect on the conversion of oil. Low oil/methanol molar ratios (1:3 and 1:12) showed low conversion (< 90%). This could be attributed to the relatively low volume proportion of methanol to triglycride in the reaction mixture, resulted in heterogeneous dispersion of the methanol. Increasing the molar ratio to 1:33 led to significant increase in the conversion percentage, which was found to be around 97%.

On the other hand, when the percentage of oil to methanol in the reaction mixture was extremely high (e.g. 1: 500), the oil becomes excessively diluted in the reaction mixture and this remarkably reduces the rate of transesterification. This is coupled with another trend is which excess methanol promotes the conversion of triglycerides into monoglycerides. The monoglycerides enhances the solubility of glycerol in the formed fatty acid methyl ester (FAME) and thus glycerolysis of FAME takes place. Thereafter, triglycerides conversion decreased. This trend was also reported in literature.[15] Based on these results, the optimal molar ratio of triglyceride and methanol in the reaction mixture for the highest biodiesel conversion was obtained at ratio 1:33.

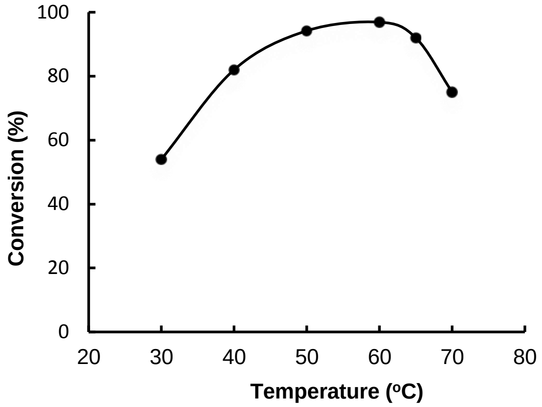


Figure 3 Effect of temperature on the conversion percentage of biodiesel for transesterification of cottonseed oil in methanol (molar ratio: oil: methanol, 1:33).

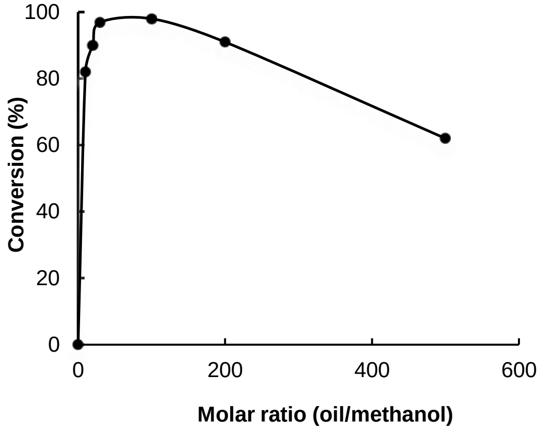


Figure 4 Effect of oil/methanol molar ration on the conversion percentage of biodiesel for transesterification of cottonseed oil (temperature: 60°C).

The GC-FID analysis was used to confirm the conversion of cottonseed oil to biodiesel. Figure 5 shows the GC chromatogram of the obtained biodiesel. The fatty acid methyl esters present in the biodiesel can be observed at peaks 2 to 6, respectively. Particularly, the most predominant methyl ester peaks are those of linoleic (53.15%), palmitic (24.74%), oleic (18.93%), stearic (2.74%) and arachidic (0.29) fatty acid methyl ester. This observation is in a good agreement with the GC results of biodiesel prepared from cottonseed oil by transesterification with methanol, using sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide as catalysts.[16]

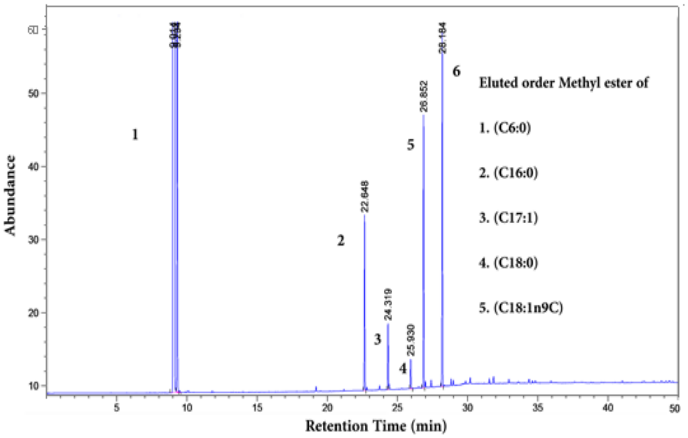


Figure 5 GC chromatogram of biodiesel obtained from cottonseed oil.

4.0 CONCLUSION

Production of biodiesel using the grafted flax fibres functionalized by amine groups and subsequent treatment with NaOH was performed successfully. The transesterification reaction temperature was found to be an important factor that can affect the conversion percentage. Highest conversion was obtained at 60 °C, nevertheless, higher temperatures led to a decrease in the conversion percentage. Moreover, the oil/methanol ratio in the reaction mixture was also found to be an important factor in the biodiesel production. At low ratio, the conversion percentages were lower than 90%, whereas the extreme increase of the methanol in the reaction led to a similar decrease in the percentage of conversion. Thus, the optimal ratio of cottonseed oil/methanol was found to be 1:33. More work is undergoing to study the effect of other reaction parameters and determine the reaction kinetics.

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