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Value-added use of residual glycerol from biodiesel production process via the optimized synthesis of alkyd resins

Faiz Miran[a], *Muhammad Waseem Mumtaz*[a], *Hamid Mukhtar*[b,*], *Muhammad Danish*[a]

[a] *Department of Chemistry, University of Gujrat, Gujrat, Pakistan*
[b] *Institute of Industrial Biotechnology, GC University, Lahore 54000, Pakistan*

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ABSTRACT

Current research work describes the value-added use of residual glycerol from biodiesel production process via the optimized synthesis of alkyd resins. Response surface methodology based on central composite response surface design was used for the optimization of alkyd resins synthesis. Various reaction parameters including phthalic anhydride to oil molar ratio, catalyst concentration, reaction temperature, reaction time and rate of stirring were optimized to obtain the optimum yield of alkyd resin by using alcoholysis–polyesterification method. The optimized reaction parameters to obtain the highest alkyd resin yield (84%) were depicted to be 0.4:1 molar ratio (phthalic anhydride to oil), 0.6% catalyst concentration, 250 °C reaction temperature, 7.5 h reaction time and 650 rpm rate of stirring. Elucidation of the chemical structure of alkyd resin was done through FT-IR analysis which confirmed the presence of ester links and aromatic C=C which resulted from polymerization reaction. Physico-chemical properties, chemical resistance and adhesive properties of synthesized alkyd resins were also evaluated which depicted that the resin films were highly resistant to brine, water and acid. These results ascertained technical compatibility of the synthesized alkyd resin for potential uses comparable to standard alkyd resins with additional eco-friendly benefits due to its biodegradability and biocompatible nature.

1. Introduction

Sustainable industrial development is solely based on the use of viable technologies with socio-chemical, economic and environmental benefits. The scientific community world-wide is searching for novel strategies and protocols to achieve optimal success and progress of various processes utilizing minimum economic resources with additional associated benefits i.e., optimal product yield and eco-friendly nature. One of the prime areas of research these days is development of alternative energy resources with objective to deal with current situation of energy discrepancy and limiting fossil waste fuel reserves. Although a significant work has been reported by the researchers regarding the optimized production of alternative fuels like biodiesel but still there are still certain questions unresolved related to the sustainability of biodiesel production technology owing to the higher prices associated with use of biodiesel. Hence further research is required to make biodiesel technology cost-effective and sustainable. One of the ways may be value-added use of residual glycerol (by-product of biodiesel production process) after refining (Yang et al., 2012). One possible valuable product that may be synthesized or manufactured using residual glycerol is biodegradable and biocompatible resins.

The resins are groups of semi-solid or solid substances that are generally transparent or translucent and yellowish to brown and are produced particularly in plant secretions or prepared by polymerization of simple molecules. They are soluble in organic solvents but not in water, and are nonconductors. The oil based biodegradable polymeric resins are called alkyd resins. The use of alkyd resins is quite common

* *Corresponding author.*
E-mail address: hamidmukhtar@gcu.edu.pk (H. Mukhtar).
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in the coating and paint industries along with essential raw materials for the manufacture of domestic and industrial finishes (Margolis, 1985; Ahmed et al., 2001; Ogunniyi and Odetoye, 2007). Almost 70% of conventional binders used in surface coating today are alkyd based (Bajpai and Seth, 2000).

Until 1927, there was no practical use of resins, when Kienle discovered a new class of alkyds, which was produced from phthalic anhydride, glycerol, and unsaturated fatty acid, such as linoleic, linolenic, and oleostearic acid (Kienle, 1929, 1949). They are more flexible and tougher than the alkyd derived from polyhydric alcohol and polybasic acid alone. General Electric Company under the name "Glypat" commercially sold first ever alkyd resin (Martens, 1961). Since then, alkyd resins have been largely used in several applications, such as plasticizer, adhesives, printing inks and molding, etc., with major use in coating field as a binder (Ahmed et al., 2001).

As nature and the amount of oils/fatty acids establish the characteristics of an alkyd resin, alkyd resins are classified in terms of oil length and oil type. The oil length is defined as the amount of oil/fatty acid present as percentage of the nonvolatile content. The complex polymer system does not describe completely by oil length but universally used throughout surface coating industry and is a convenient method of classification for alkyds. On the basis of oil length, alkyds can be classified as; short oil alkyd (oil content less than 45% w/w, medium oil alkyd (oil content 45–55% w/w), long oil alkyd (oil content greater than 55% w/w). The alkyd resins are polymerized and cross linked to such a degree that they remain still soluble in a given solvent during manufacturing (Paul, 1985). The resins are then left to cure after applying the suitable solvent. In curing both esterification and fatty acid crosslink formation processes are involved (Wicks et al., 1999). And based on final properties of alkyd resins produced, each process has advantages and disadvantages over the others.

Therefore taking into consideration its significance, the present study was planned with the objectives including value added use of glycerol byproduct of biodiesel production process, alkyd resin production by alcoholysis followed by esterification of oil, optimization of alkyd resin production using RSM and characterization of synthesized alkyd resin. This novel route will not only make the biodiesel technology cost- effective but may also result in the initiation of new industrial applications.

2. Materials and methods

2.1. Procurement of raw materials

Sunflower oil was procured from the local market situated in District Gujrat, Pakistan, whereas crude glycerol (by-product of biodiesel) was obtained from the laboratory of Chemistry Department, University of Gujrat. The glycerol was produced as a by-product as result of transesterification of oil for biodiesel production and was purified before use. All the chemicals and reagents including phthalic anhydride, xylene and lithium hydroxide used in the presented study were of research grade obtained from Merck Chemicals, Darmstadt, Germany.

2.2. Quality of evaluation feedstock

2.2.1. Physico-chemical characterization of oil

Quality of under study oil was evaluated by estimating its physico-chemical characteristics viz., acid value, peroxide value, saponification value, iodine value, refractive index, unsaponofiable matter, specific gravity and density using the standard AOCS analytical method (American Oil Chemists' Society (AOCS), 1997).

2.2.2. Purification & characterization of crude glycerol (residue of biodiesel process)

Crude glycerol was first purified as it was highly impure due the presence of excess methanol, residual catalyst, esters, water and unreacted oil etc. The pH of the crude glycerol was in between 11–12 (byproduct of biodiesel production process catalyzed by some alkaline catalyst) and dark brown in color. The crude glycerol was purified before use by using the method of glycerol purification reported by Hidawati and Sakinah (2011) and Xiao et al. (2013).

2.2.3. FT-IR spectroscopic and GC–MS analysis of feedstock

The feedstock, both the vegetable oil and the glycerol were analyzed using FT-IR spectroscopy. The FTIR spectroscopic analysis was performed with Thermo Fisher Nicolet IS10 FT-IR over a scanning range of 500–4000 cm^{-1}. For compositional (fatty acid profile) analysis, the sunflower oil was subjected to GC–MS analysis. Gas Chromatographic system 6890 N equipped with an inert XL Mass detector and capillary column (100 m × 0.25 mm & film thickness 0.20 μm) was used. Fatty acid methyl esters were identified by comparison between the relative retention times of each FAMEs and those of standards of FAMEs (Sigma Chemical Co., St Louis, MO, USA) and reported as their percentage composition.

2.3. Production of alkyd resins

Alkyd resin was prepared from the glycerol, sunflower oil and phthalic anhydride using lithium hydroxide (LiOH) as catalyst. Following reaction parameters; phthalic anhydride to oil molar ratio (A), catalytic concentration (B), reaction temperature (C), reaction time (D) and rate of stirring (E) were optimized for the ranges i.e., 0.1:1– 0.4:1, 0.01–0.1 wt%, 200–300 °C, 05–10 h and 500–800 rpm, respectively. All the experiments were performed in a four necked round bottom flask of capacity 1000 ml equipped with a mechanical stirrer and agitation speed of 500–800 rpm, thermometer, nitrogen gas inlet and dean & stark trap carrying a water condenser. Synthesis of the alkyd resin was carried out in two steps i.e., alcoholysis and esterification.

2.3.1. Alcoholysis

In this step, monoglycerides were first synthesized by reacting sunflower oil with glycerol. Alcoholysis of oil was carried out using specified levels of lithium hydroxide (LiOH) 0.01–0.1 wt%, rate of stirring 500–800 rpm and reaction temperature 200–300 °C as per Central Composite Response Surface Design (CCRD). Alcoholysis was carried out under inert atmosphere with N_2 to prevent discoloration of product. Completion of alcoholysis was checked by dissolving one part of the reaction mixture with three parts of anhydrous methanol resulting into a clear solution. After performing alcoholysis the reaction temperature was maintained at 180 °C before the start of next stage of reaction.

2.3.2. Esterification

In this step, the phthalic anhydride mole ratio (phthalic anhydride to oil 0.1:1–0.4:1) and xylene were introduced to the reaction mixture and reaction temperature was raised up to temperature range i.e., 230–250 °C and then the esterification reaction was monitored by estimating the acid value periodically, until it dropped to a level below 10. After completing esterification step alkyd resin was obtained and subjected