UNIVERSITI TEKNOLOGI MARA

EPOXIDATION OF UNSATURATED FATTY ACIDS IN CASTOR OIL WITH A SULFATE-IMPREGNATED ZEOLITE, ZSM-5/H2SO4 CATALYST

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ABSTRACT

Catalysts are essential in modern chemical processes to enhance reaction efficiency. Traditional homogeneous catalysts such as sulfuric acid have been widely used in epoxidation reactions due to their high Relative Conversion Oxirane (RCO) .These catalysts offer excellent contact with reactants, promoting efficient mass transfer and reaction kinetics, which often results in higher product yields. However, their corrosive nature and the generation of hazardous byproducts lead to environmental and safety concerns. Previous studies have demonstrated that while homogeneous catalysts provide superior oxirane yields, they are less favorable in terms of catalyst recovery, process sustainability, and environmental impact. In contrast, heterogeneous catalysts like zeolites (ZSM-5) offer greater sustainability, ease of separation, and reusability, but they often lead to lower product yields due to diffusional limitations and reduced active site accessibility. To address these limitations, this study investigated the use of sulfate-impregnated ZSM-5 (ZSM-5/H2SO4) to maintain environmental sustainability. To date, there are no reported studies on sulfate-impregnated zeolites applied specifically to epoxidation of castor oil reactions, marking this as a novel research area. This research aimed to optimize catalyst conditions preparation by determining the ideal impregnation temperature, acid concentration, and calcination temperature. Using the One Factor At a Time (OFAT) method, optimal conditions that yield highest RCO were identified at impregnation temperature of 25 °C, sulfuric acid concentration of 0.3 M, and a calcination temperature of 550 °C. RCO was calculated following the AOCS Official Method Cd-9-57. The ZSM-5/H2SO4 further applied to epoxidation process. While epoxidation industries reliant on petroleum are facing mounting sustainability challenges, which leads to a driving of renewable and bio-based alternatives. This study utilized castor oil as a renewable feedstock to reduce dependency on non-renewable resources and minimize environmental impact. By applying 1 wt.% of the ZSM-5/H2SO4, the ideal reaction conditions were established as a 1:1:1 molar ratio of acetic acid and hydrogen peroxide to ethylenic unsaturation, a reaction temperature of 65 °C, and a stirring speed of 200 rpm using Taguchi optimization method. Under these conditions, a maximum RCO of approximately 62% was achieved. Catalyst recyclability was also evaluated, where the RCO declined to 46% after the first cycle and after three cycles, the RCO decreased to 10%. Furthermore, the study explored different hydroxyl reagents for polyol synthesis, demonstrating that both reagent selection and molar ratio significantly affect hydroxyl values. At a reagent ratio of 1:1.5, the hydroxyl values obtained were as follows: ECO:Peracetic Acid (79.3 mg KOH/g), in situ hydrolysis (85 mg KOH/g), ECO:Hydrogen Peroxide (89.1 mg KOH/g), ECO:Water (108.1 mg KOH/g), ECO:Methanol (127.9 mg KOH/g), and ECO:Acetic Acid (139.4 mg KOH/g). These results indicated that polyols with different hydroxyl values can be synthesized by adjusting reagent ratios. To enhance process modeling, a novel hybrid kinetic modeling approach combining Particle Swarm Optimization and Simulated Annealing were developed in MATLAB R2023a. This hybrid model successfully addressed the issue of local optima entrapment and demonstrated superior performance, achieving a coefficient of determination (R^2) of 0.9961, outperforming standalone Particle Swarm Optimization (0.9836) and Simulated Annealing (0.8459) models.

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CHAPTER 1
INTRODUCTION

1.1 Introduction

As the world seeks stable socio-economic development, petroleum plays a pivotal role due to its broad influence on economic, social, and environmental systems [1]. However, the petroleum is non-renewable and depleting rapidly due to economic and population growth [2].Therefore, it is important to ensure a clean, renewable, affordable, and sufficient energy source that reduces dependency on finite fossil-based resources. Advancements in technology have introduced greener approaches to synthesize epoxidized resin using vegetable oil [3]. Due to their unsaturated structure, vegetable oils are chemically modifiable through epoxidation and serve as biodegradable, renewable feedstocks for industrial chemicals [4].

Among vegetable oils, castor oil stands out due to its high content of ricinoleic acid that contributes significantly to its chemical versatility [3], [5]. Castor oil is derived from the seeds *oiRicinus communis,* a member of the *Euphorbiaceae* spurge family [6]. It can thrive in various climates, including Malaysia where castor plant cultivation has been studied in Sabah [7]. Despite high demand, castor oil production in Malaysia is currently classified as a minor crop oil. Castor plants prefer temperatures between 20 and 25 °C for optimal growth, while temperatures below 12 °C or above 38 °C can impact germination and yield [8].

Epoxidation of castor oil, typically using organic peracids with hydrogen peroxide in the presence of catalysts converts carbon-carbon double bonds in unsaturated fatty acids into oxirane rings [9]. The epoxidation process can utilize a variety of reagents and catalysts, which may be classified as either homogeneous (e.g., mineral acids) or heterogeneous (e.g., solid-supported acids or metal oxides) [10], [11], [12]. Homogeneous catalysts typically yield higher relative conversion (RCO) values than heterogeneous catalysts [13]. However, their use is often associated with toxicity, environmental concerns, and a lack of reusability. In contrast, heterogeneous catalysts are more environmentally friendly and reusable, though they often result in lower conversion efficiencies. Reaction conditions such as temperature, stirring speed, reaction time, and the ratio of reagents, as well as the choice of catalyst, are critical